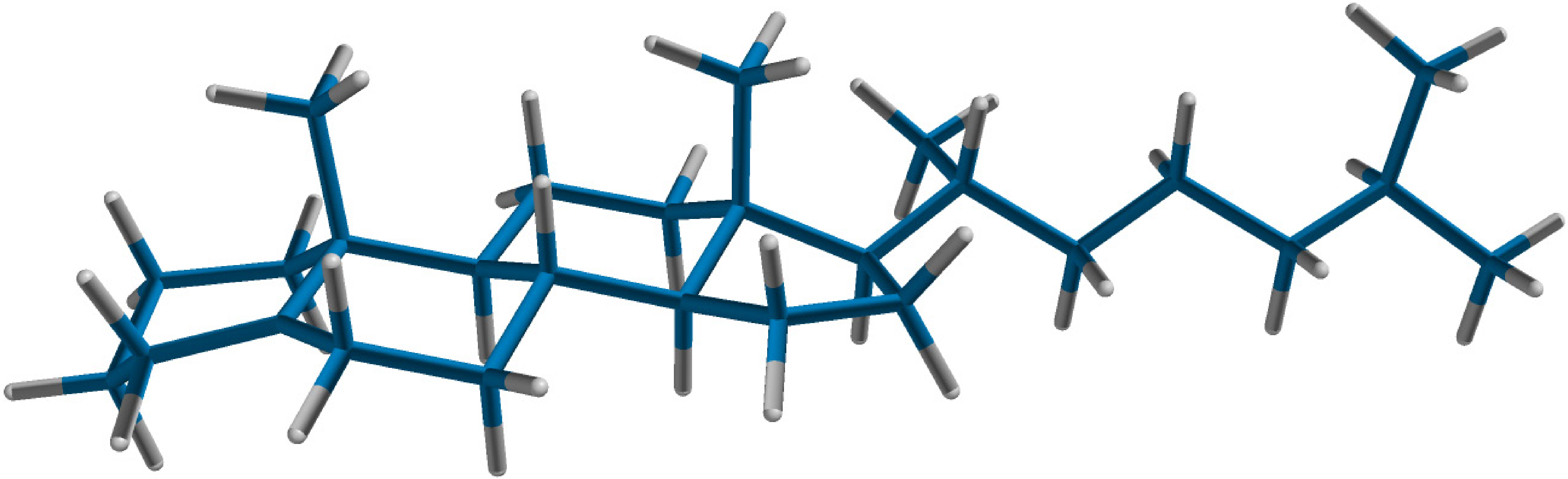
4

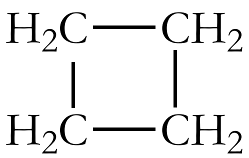
ALKANES AND CYCLOALKANES
STRUCTURES AND REACTIONS



4.1 CLASSES OF HYDROCARBONS

$CH_3—CH_2—CH_2—CH_3$

butane

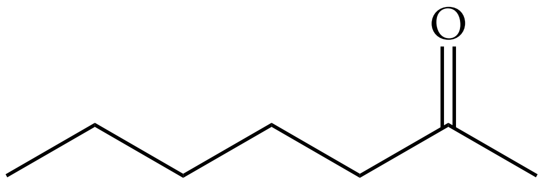


cyclobutane

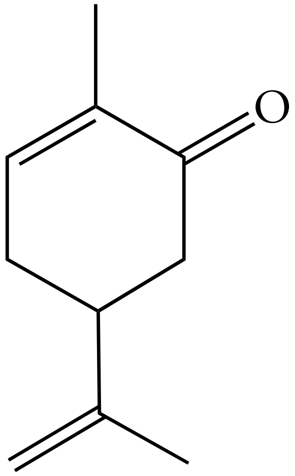
an acyclic compound

a cyclic compound

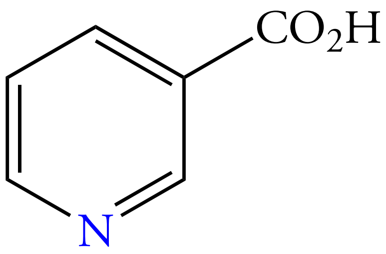
a heterocyclic compound



2-heptanone
in oil of cloves



carvone
in spearmint oil



nicotinic acid
a B vitamin

4.2 ALKANES

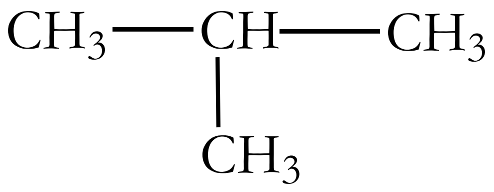
$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

octane

(a normal alkane)

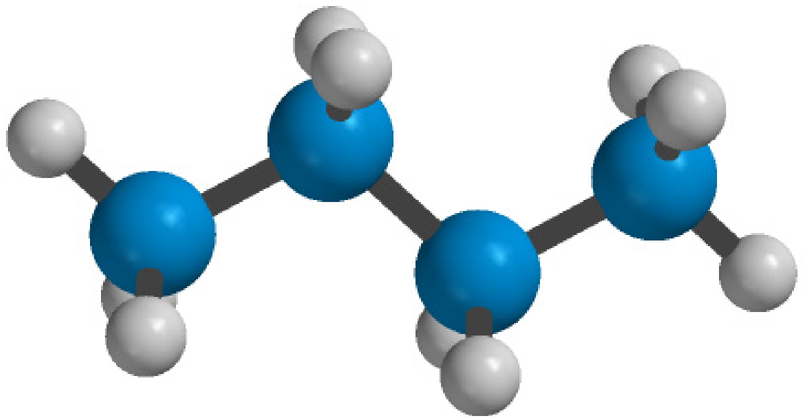
$$CH_3{-}CH_2{-}CH_2{-}CH_3$$

butane

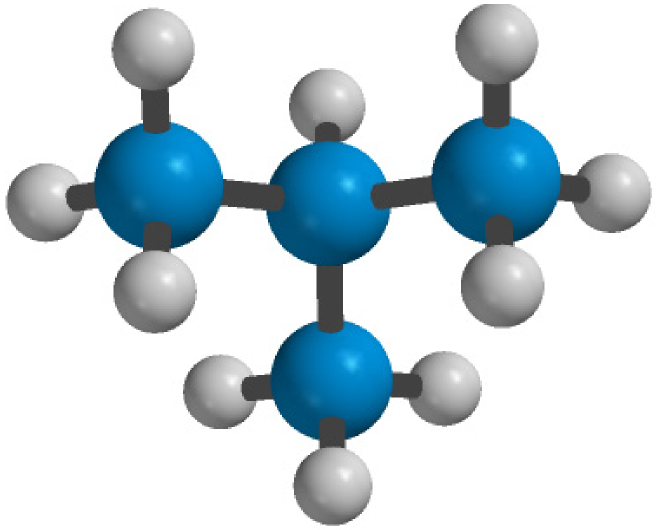


$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$$

isobutane



butane

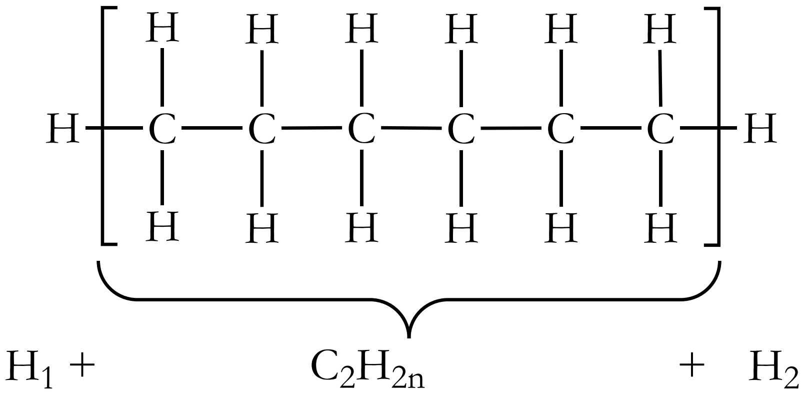


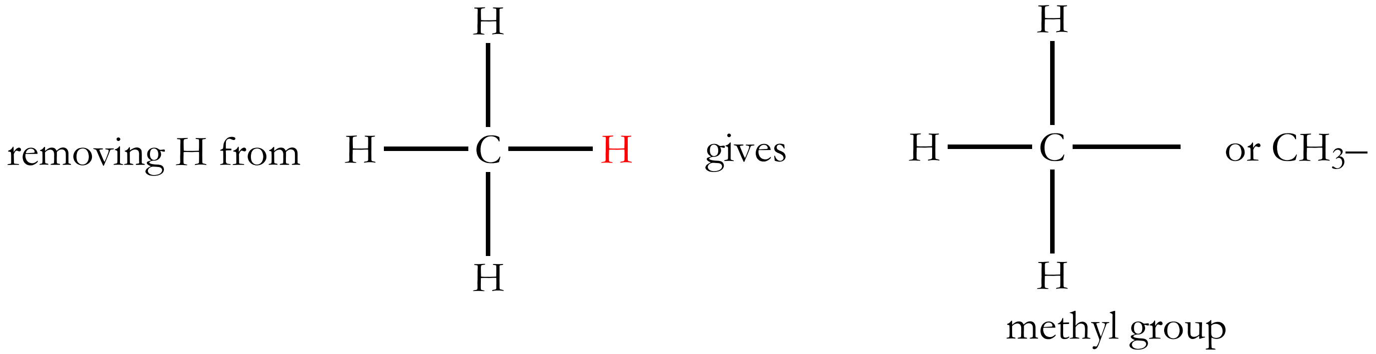
isobutane

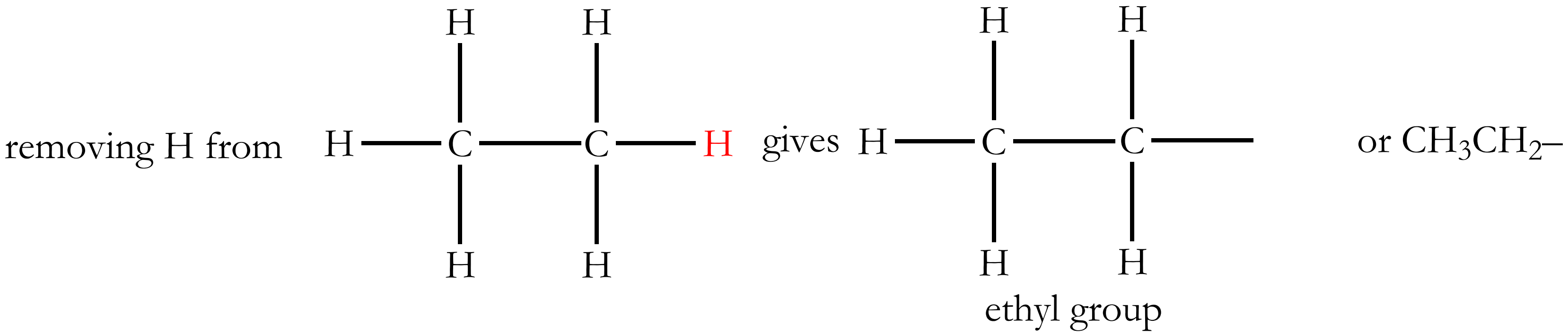
4.2 ALKANES

Table 4.1
Names of Normal Alkanes

Number of Carbon Atoms	*Name*	*Molecular Formula*
1	methane	CH_4
2	ethane	C_2H_6
3	propane	C_3H_8
4	butane	C_4H_{10}
5	pentane	C_5H_{12}
6	hexane	C_6H_{14}
7	heptane	C_7H_{16}
8	octane	C_8H_{18}
9	nonane	C_9H_{20}
10	decane	$C_{10}H_{22}$
11	undecane	$C_{11}H_{24}$
12	dodecane	$C_{12}H_{26}$
13	tridecane	$C_{13}H_{28}$
14	tetradecane	$C_{14}H_{30}$
15	pentadecane	$C_{15}H_{32}$
16	hexadecane	$C_{16}H_{34}$
17	heptadecane	$C_{17}H_{36}$
18	octadecane	$C_{18}H_{38}$
19	nonadecane	$C_{19}H_{40}$
20	eicosane	$C_{20}H_{42}$







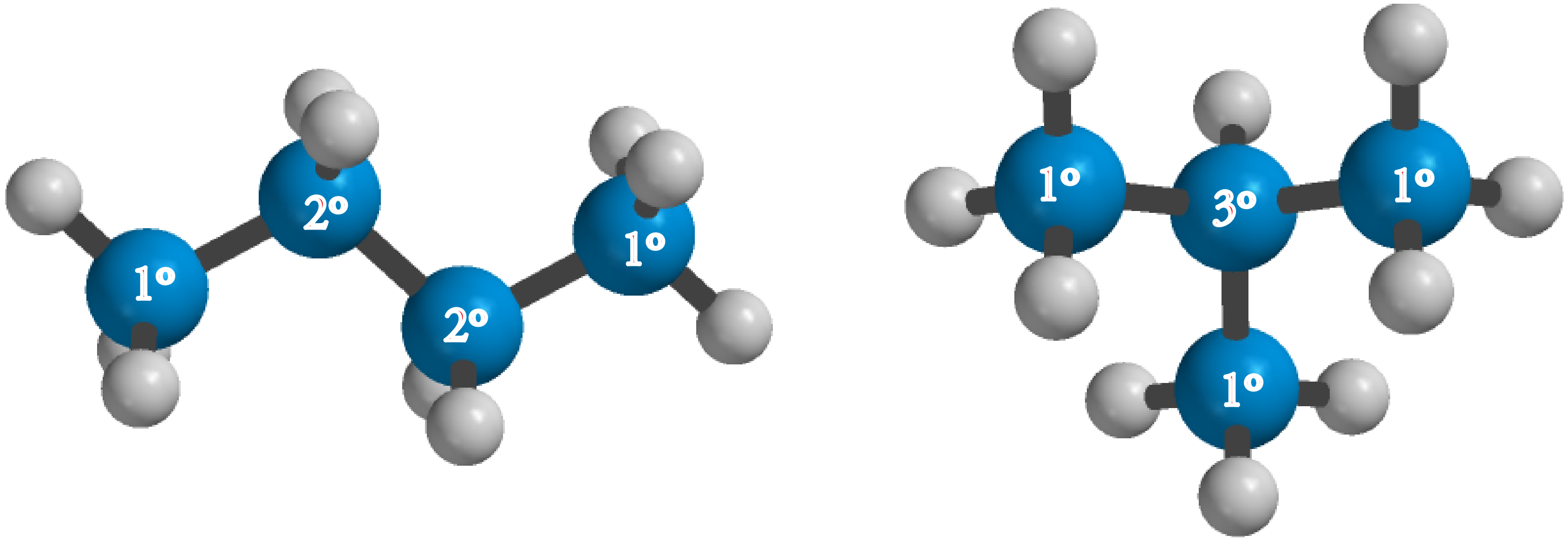
4.2 ALKANES

Classification of Carbon Atoms

Figure 4.1Classification of Carbon Atoms

(a) The terminal carbon atoms of butane are primary (1°); they are bonded directly to one other carbon atom. The internal carbon atoms are secondary; they are bonded to two carbon atoms.

(b) The terminal carbon atoms of iso-butane are primary; they are bonded to one other carbon atom. The internal carbon atom is tertiary (3°); it is bonded to three carbon atoms.



butane
(a)

isobutane
(b)

4.3 NOMENCLATURE OF ALKANES

Table 4.2
Number of Alkane Isomers

Molecular Formula	Number of Isomers
CH_4	1
C_2H_6	1
C_3H_8	1
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{20}H_{42}$	336,319
$C_{30}H_{62}$	4,111,846,763
$C_{40}H_{82}$	62,491,178,805,831

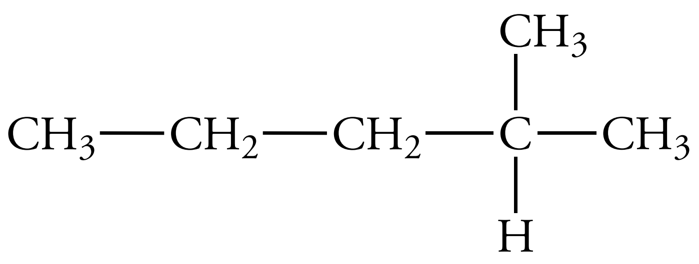
4.2 ALKANES

IUPAC Rules for Naming Alkanes

Prefix — Parent — Suffix

The IUPAC rules for naming alkanes are as follows:

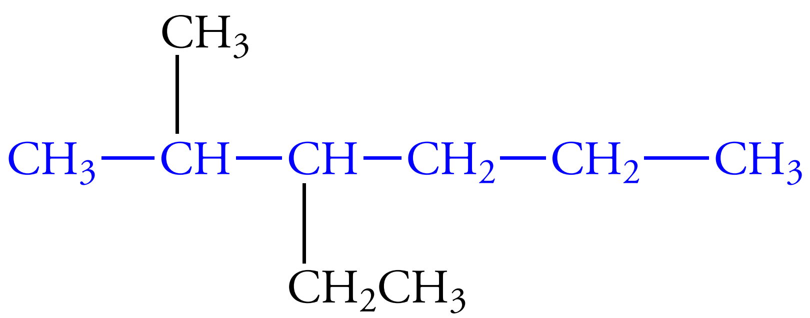
1. The longest continuous chain of carbon atoms is the parent.



$$CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_3$$

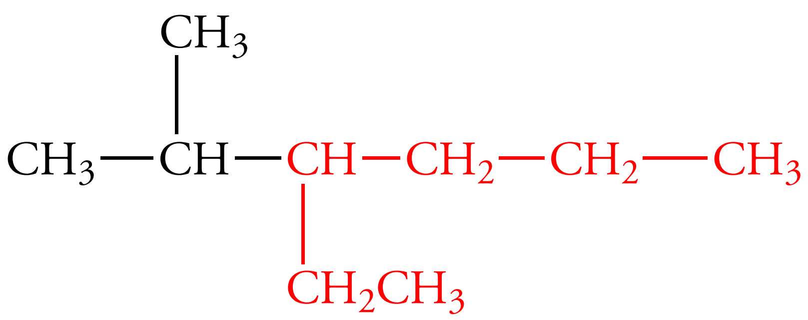
The parent chain contains five carbons.

If two possible parent chains have the same number of carbon atoms, the parent is the one with the larger number of branch points.



$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

The parent chain has six carbons with two branches: a methyl group and an ethyl group.



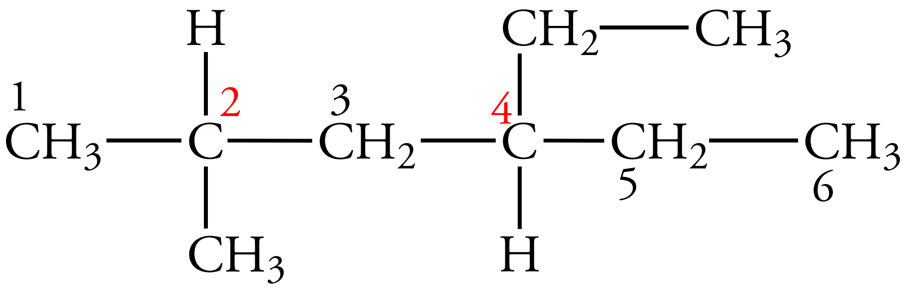
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

The six carbon parent chain with one branch is not correct.

4.2 ALKANES

IUPAC Rules for Naming Alkanes

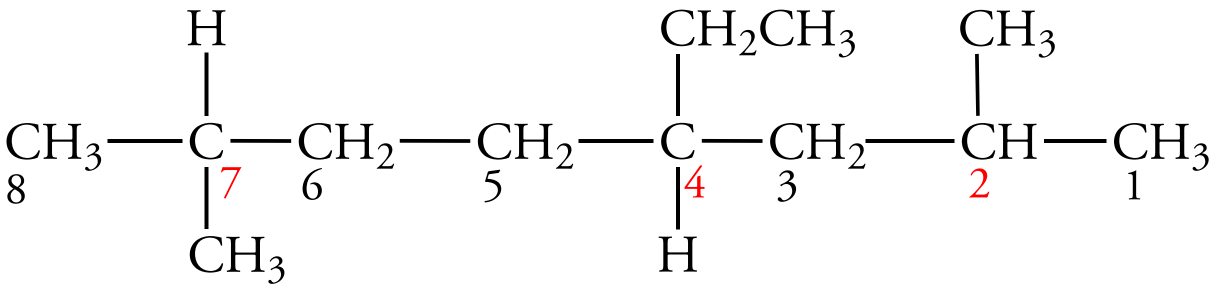
2. Number the carbon atoms in the longest continuous chain starting from the end of the chain nearer the first branch.



$CH_3-CH(CH_3)-CH_2-CH(CH_2CH_3)-CH_2-CH_3$

The parent chains contains six carbons, so it is a hexane with two branches: a methyl group at C-2 and an ethyl group at C-4.

If the first branch occurs at an equal distance from each end of the chain, number from the end that is nearer the second branch.



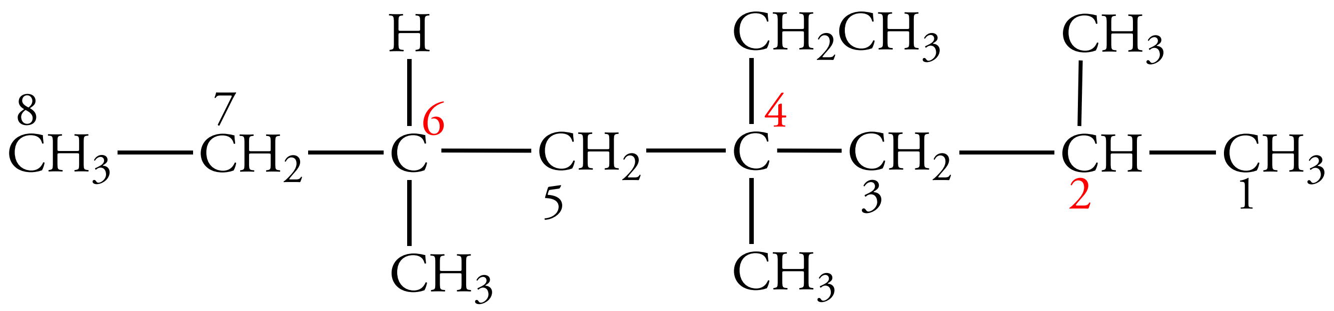
$CH_3-CH(CH_3)-CH_2-CH_2-CH(CH_2CH_3)-CH_2-CH(CH_3)-CH_3$

The parent has eight carbons, so it is an octane. It has methyl groups at C-2 and C-7 and an ethyl group at C-4.

4.2 ALKANES

IUPAC Rules for Naming Alkanes

3. Each branch or substituent has a number that indicates its location on the parent chain. When two substituents are located on the same carbon atom, each must be assigned the same number.



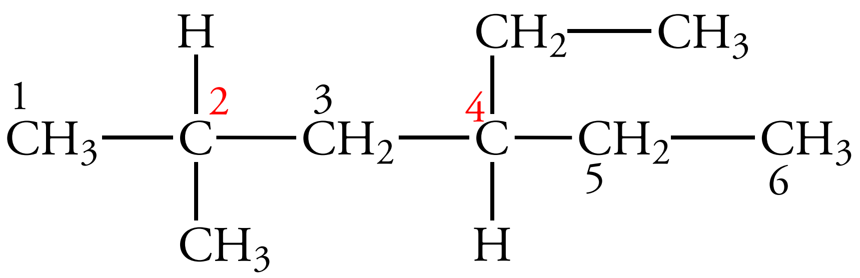
$$\overset{8}{CH_3}-\overset{7}{CH_2}-\underset{CH_3}{\overset{H}{C}}-\underset{5}{CH_2}-\underset{CH_3}{\overset{CH_2CH_3}{C}}-\underset{3}{CH_2}-\overset{CH_3}{\underset{2}{CH}}-\underset{1}{CH_3}$$

This octane has methyl groups at C-2, C-4, and C-6, and an ethyl group at C-4.

4.2 ALKANES

IUPAC Rules for Naming Alkanes

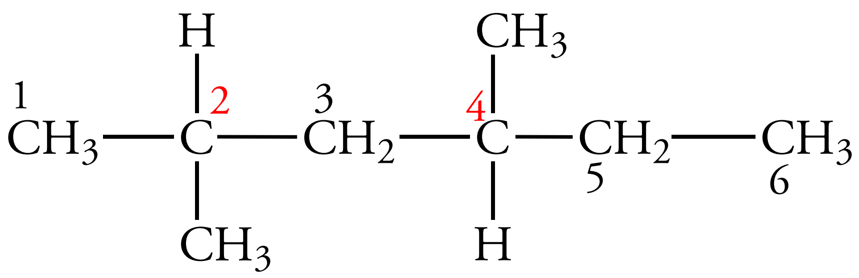
4. The number for the position of each alkyl group is placed immediately before the name of the group and is joined to the name by a hyphen. Alkyl groups and halogen atoms are listed in alphabetical order.



$CH_3-CH(CH_3)-CH_2-CH(CH_2-CH_3)-CH_2-CH_3$

The name of this compound is 4-ethyl-2-methylhexane, *not* 2-methyl-4-ethylhexane.

Two or more groups of the same type are indicated by the prefixes di, tri, tetra-, and so forth. The numbers that indicate the locations of the branches are separated by commas.



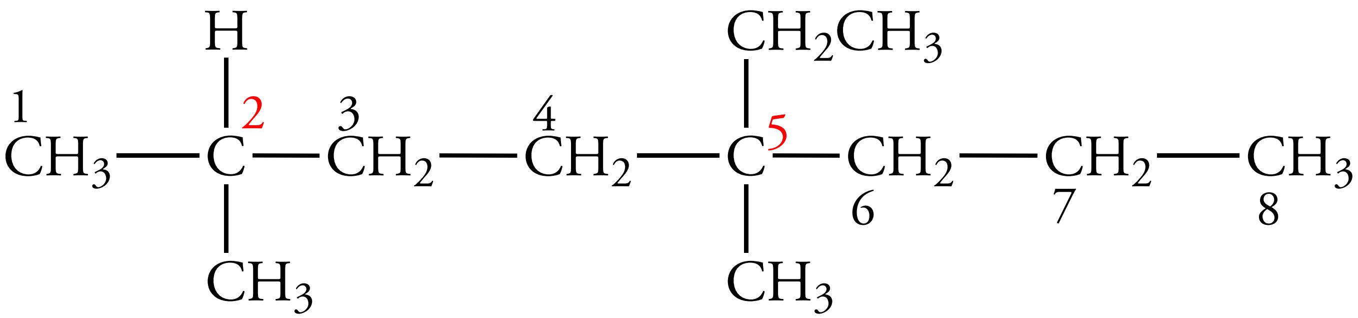
$CH_3-CH(CH_3)-CH_2-CH(CH_3)-CH_2-CH_3$

The name of this compound is 2,4-dimethylhexane

4.2 ALKANES

IUPAC Rules for Naming Alkanes

5. The prefixes di, tri, tetra-, and so forth, do not alter the alphabetical ordering of the alkyl groups.



$$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2-CH_2-\underset{CH_3}{\overset{CH_2CH_3}{C}}-CH_2-CH_2-CH_3$$

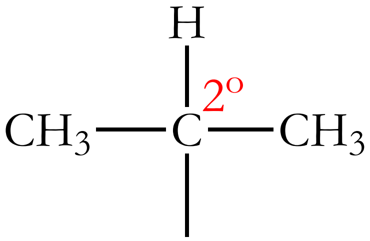
The name of this compound is 5-ethyl-2,5-dimethyloctane, *not* 3,5,-dimethyl-5-ethyloctane.

4.2 ALKANES

Names of Alkyl Groups

$CH_3-CH_2-\overset{1^\circ}{CH_2}-$

n-propyl

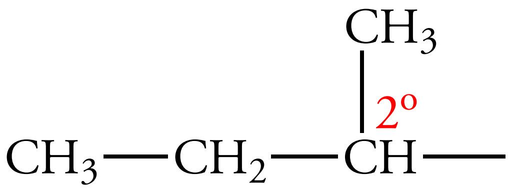


$CH_3-\underset{|}{\overset{\overset{H}{|}}{C}}{}^{2^\circ}-CH_3$

iso-propyl

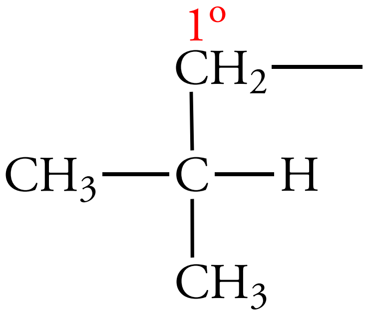
$CH_3-CH_2-CH_2-\overset{1^\circ}{CH_2}-$

n-butyl



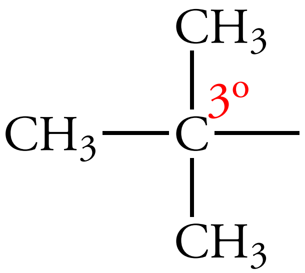
$CH_3-CH_2-\overset{\overset{CH_3}{|}\,2^\circ}{CH}-$

sec-butyl



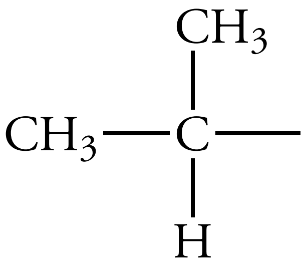
$\begin{array}{c} \overset{1^\circ}{CH_2}- \\ | \\ CH_3-C-H \\ | \\ CH_3 \end{array}$

iso-butyl



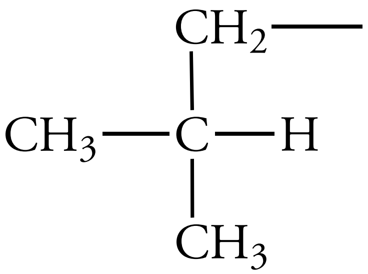
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}\,3^\circ}{C}}-$

tert-butyl



$CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-$

2-methylethyl
(isopropyl)



$\begin{array}{c} CH_2- \\ | \\ CH_3-C-H \\ | \\ CH_3 \end{array}$

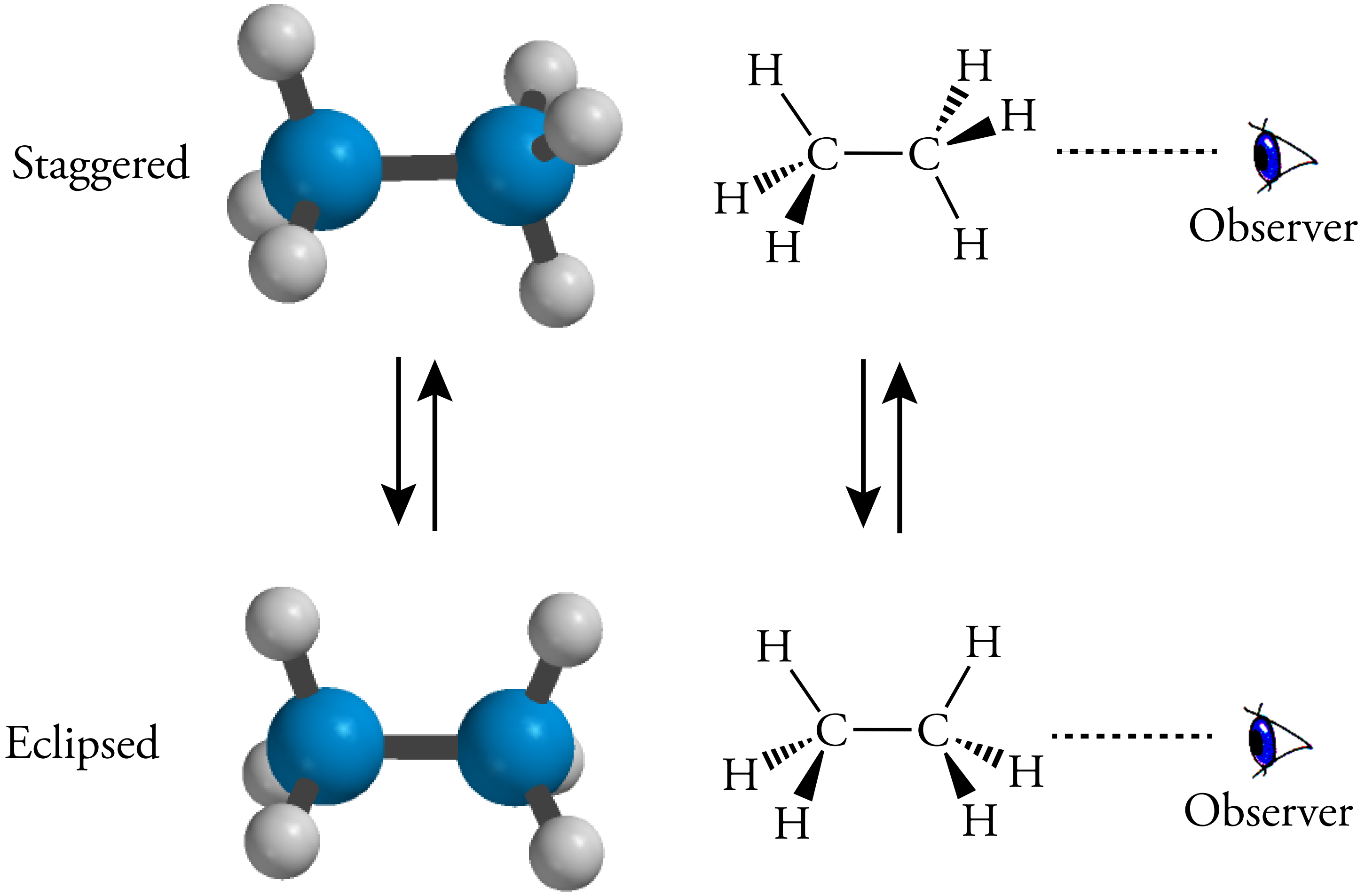
2-methylpropyl
(sec-butyl)

4.4 CONFORMATIONS OF ALKANES

Conformations of Ethane

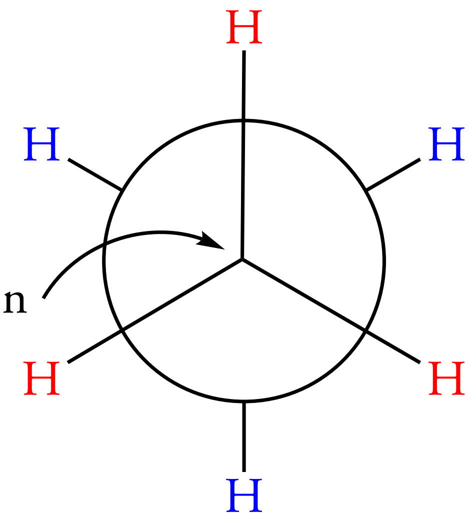
Figure 4.2 Conformations of Ethane

Rotating the methyl group on the right by 60° converts a staggered conformation into an eclipsed conformation. Viewing the carbon-carbon bond end-on in the eclipsed conformation we would see the carbon atom and three hydrogens of the carbon on the right. The left carbon and its three hydrogens would be hidden.



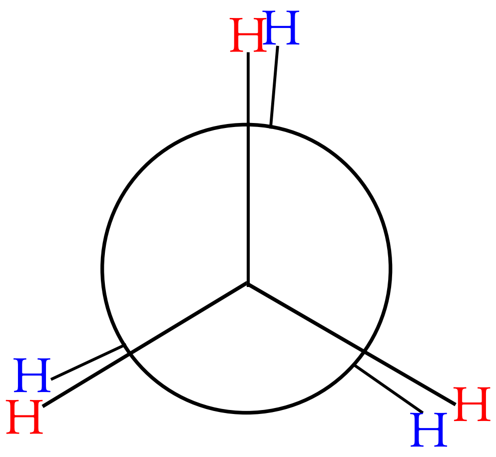
4.4 CONFORMATIONS OF ALKANES

Newman Projection Formulas



front carbon hides back carbon

Newman projection of staggered ethane



eclipsed ethane conformation

4.4 CONFORMATIONS OF ALKANES

Barrier to Rotation in Ethane

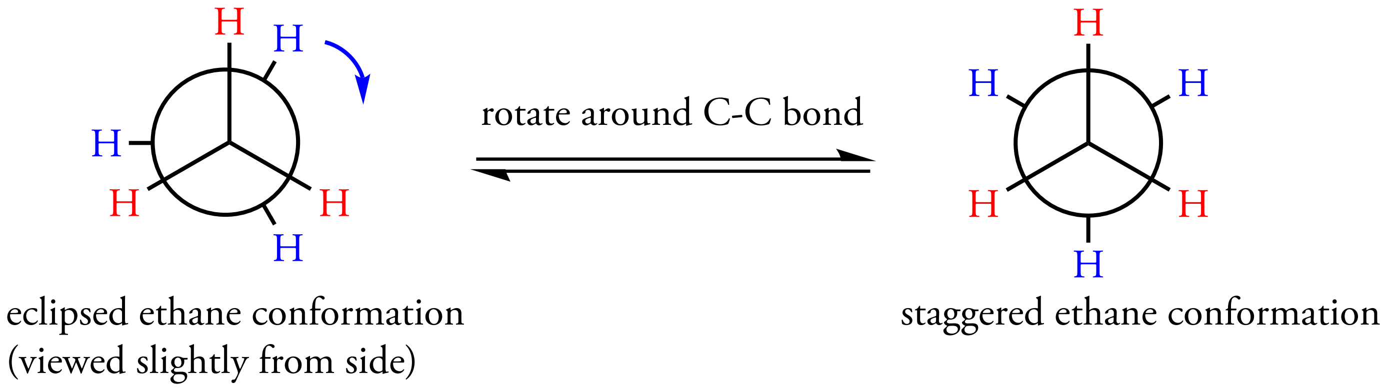
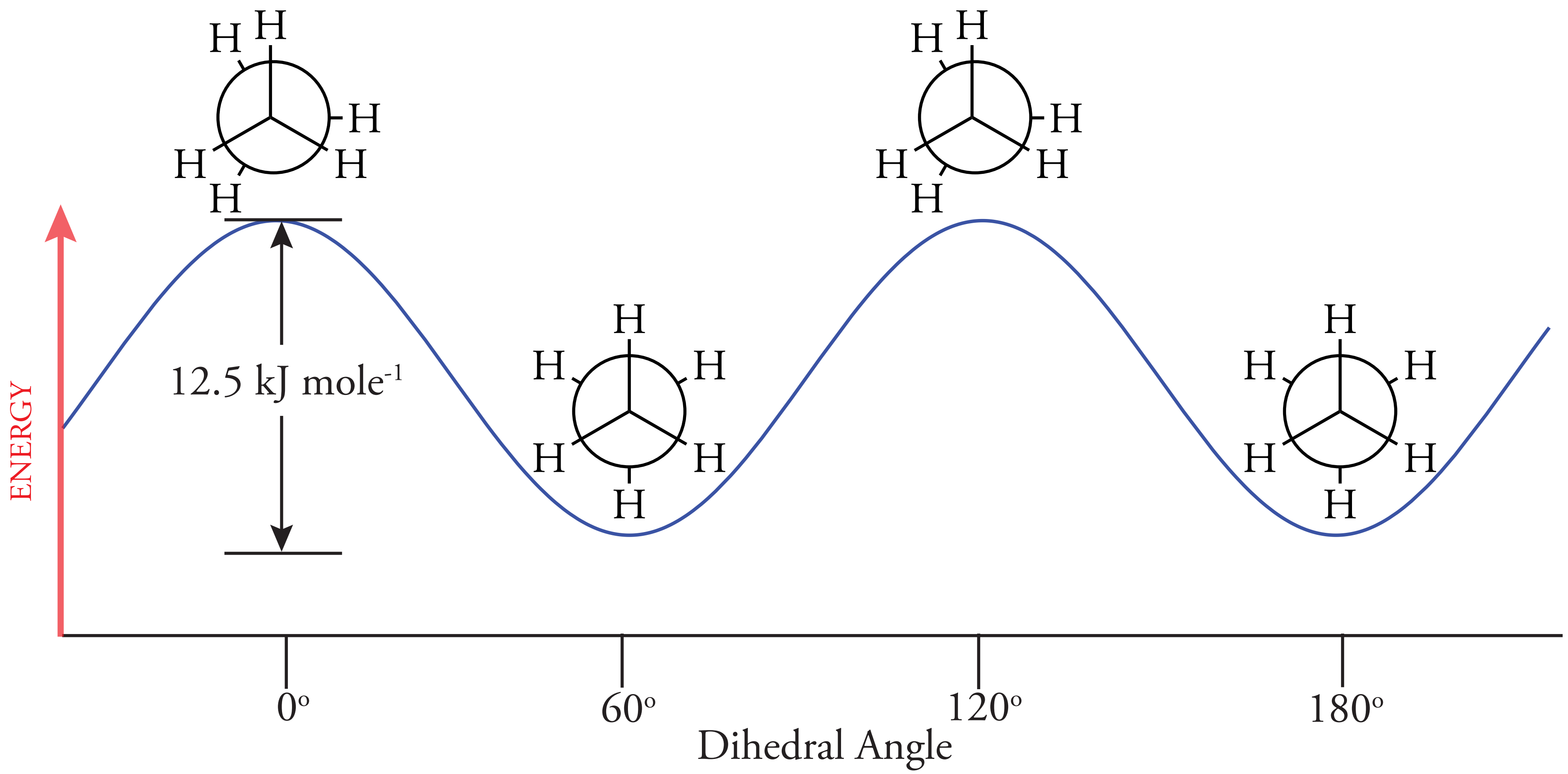
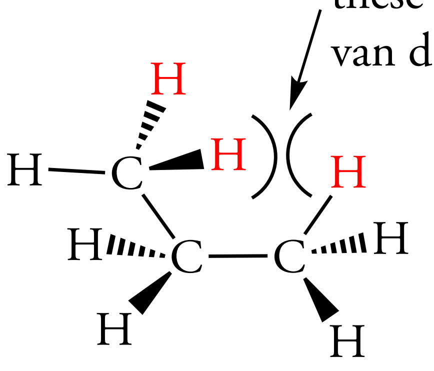


Figure 4.3 Rotational Barrier for Conformations of Ethane
Rotation around the carbon-carbon bond of ethane in 60° increments gives a series of alternating eclipsed and staggered conformations. The eclipsed conformation is 12.6 kJ mole^{-1} higher in energy than the staggered conformation. Each hydrogen-hydrogen interaction contributes 4.2 kJ mole^{-1} to the total energy barrier.

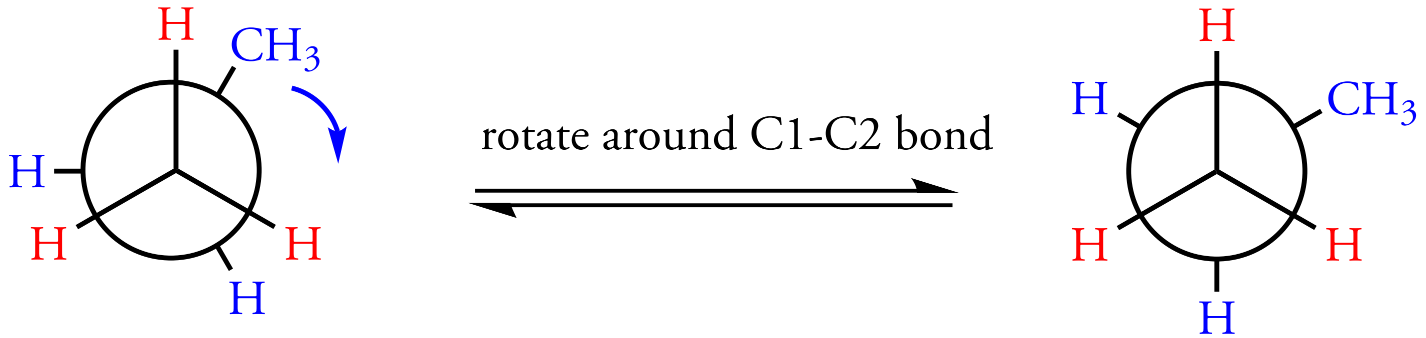


4.4 CONFORMATIONS OF ALKANES

Conformations of Propane



these hydrogens are in van der Waals contact



rotate around C1-C2 bond

eclipsed propane conformation
(viewed slightly from side)

staggered propane conformation

Table 4.3

Van der Waals Radii

Group	**Radius (pm)**
CH_3	200
CH_2	200
Br	195
Cl	180
F	135
H	120

4.4 CONFORMATIONS OF ALKANES

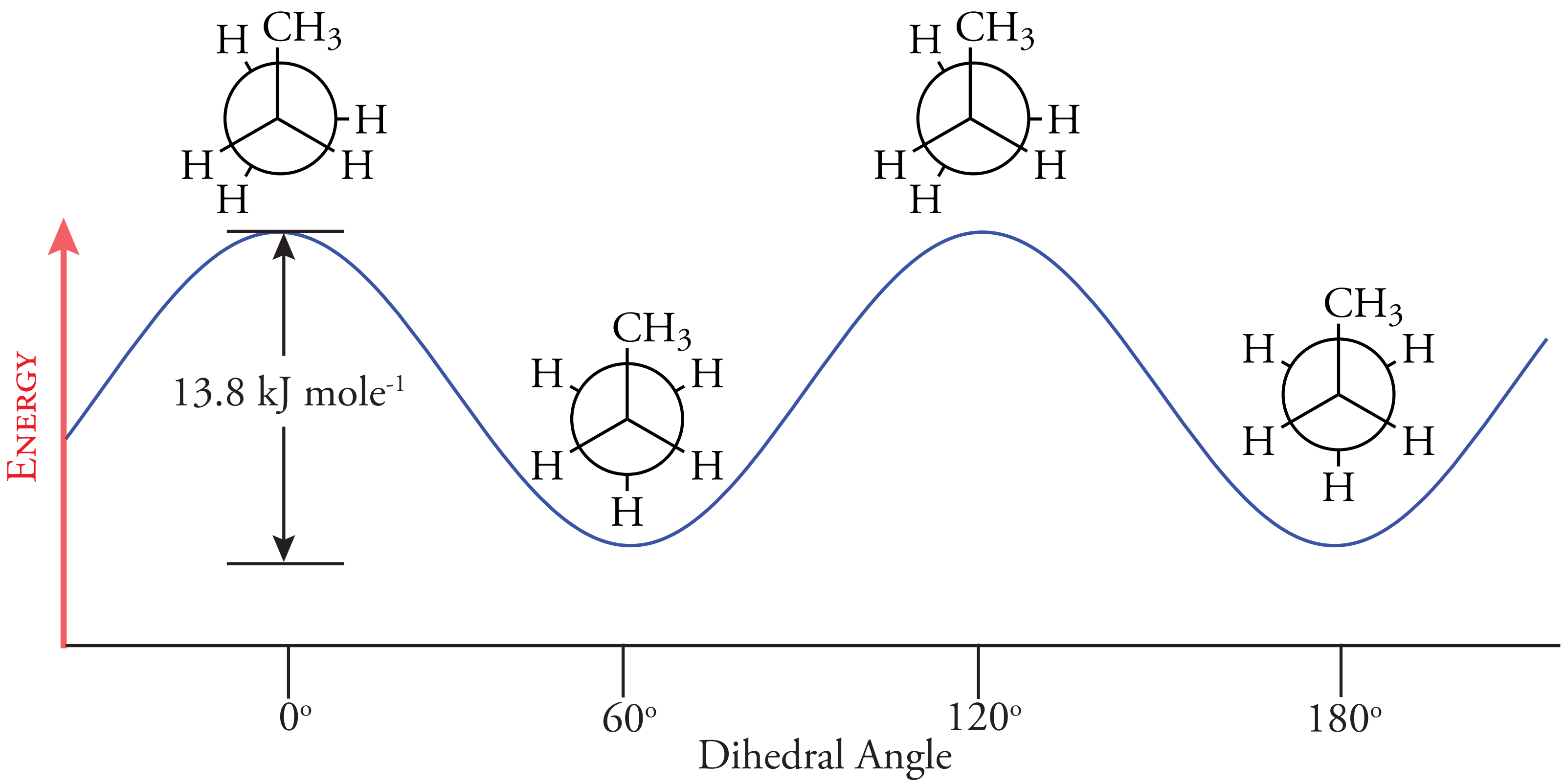
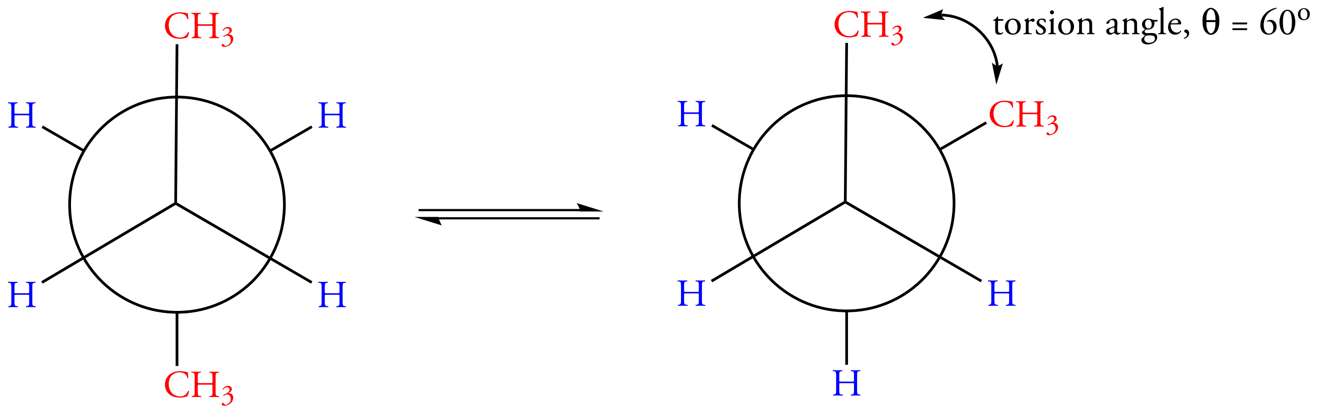


Figure 4.4 Rotational Barrier for Conformations of Propane

Rotation around the carbon–carbon bond of propane in 60° increments starting from an eclipsed conformation gives a series of alternating eclipsed and staggered conformations. The eclipsed conformation is 13.8 kJ mole^{-1} higher in energy than the staggered conformation.

4.4 CONFORMATIONS OF ALKANES

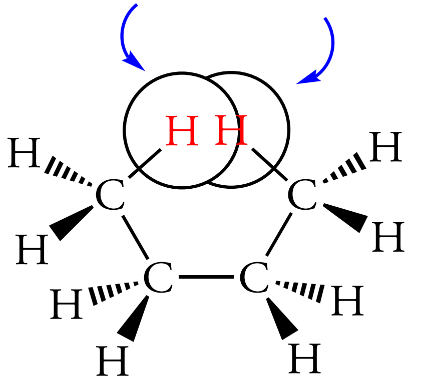
Conformations of Butane



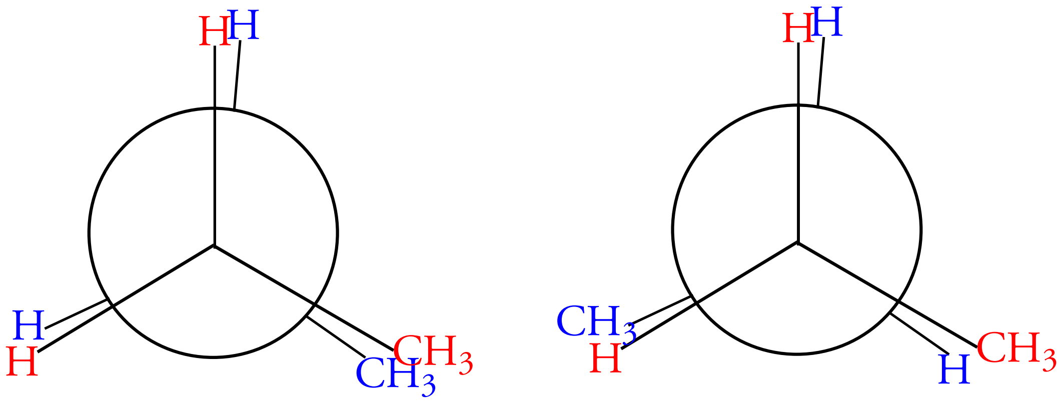
anti butane

gauche butane

The van der Waals radii of these hydrogens overlap.



eclipsed butane

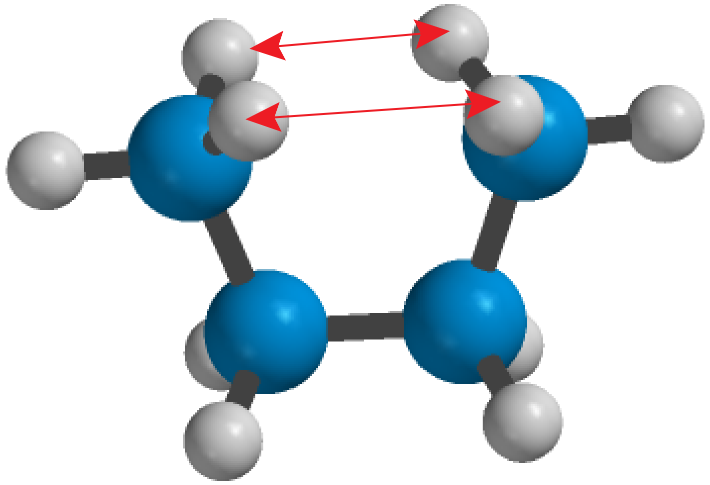


$\theta = 0^\circ$

$\theta = 120^\circ$

eclipsed butane conformations

van der walls repulsion

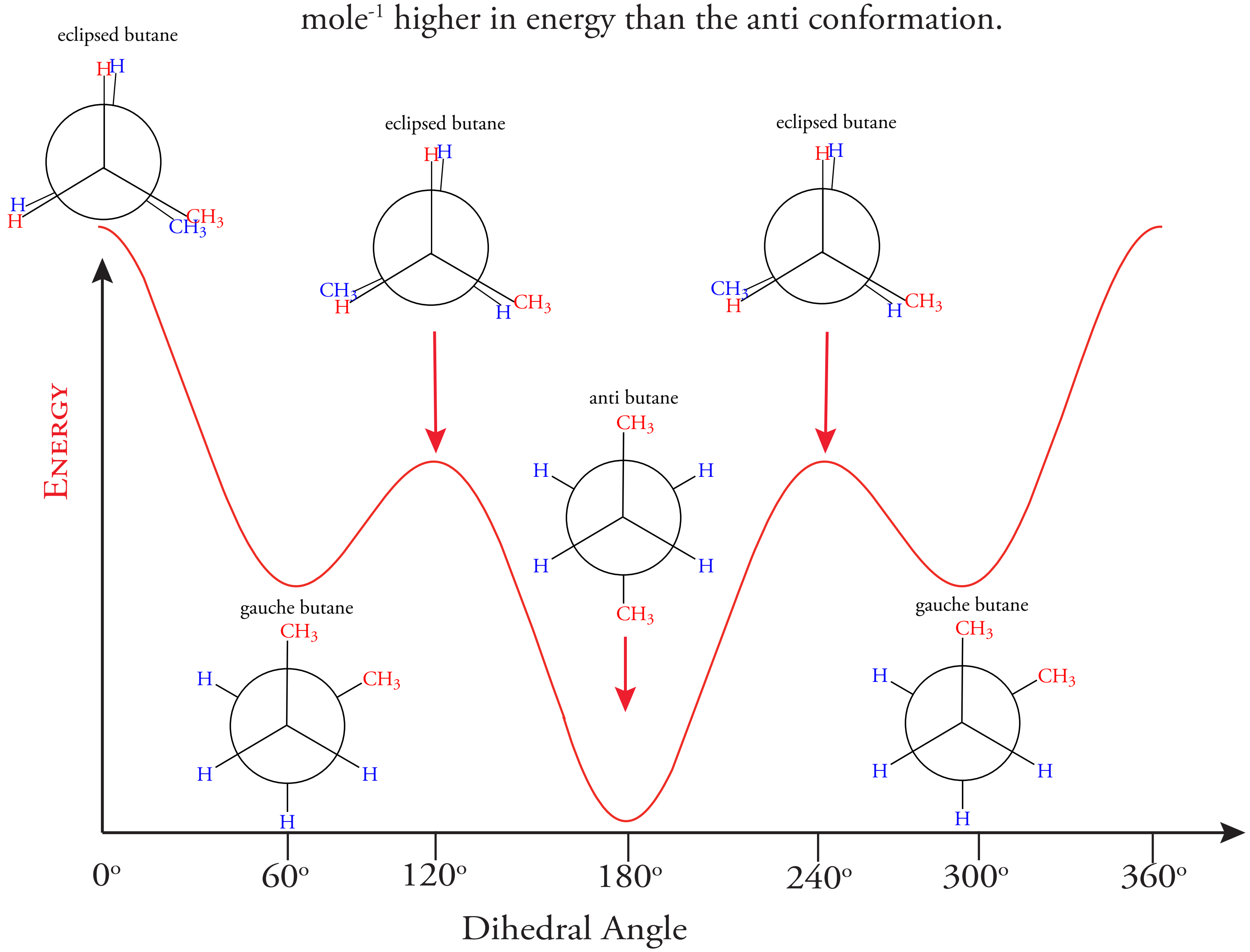


eclipsed butane

4.4 CONFORMATIONS OF ALKANES

Figure 4.5 Rotational Barrier for Conformations of Butane

Rotation around the C2-C3 bond of butane starting from a methyl-methyl eclipsed conformation gives two nonequivalent eclipsed and two nonequivalent staggered conformations. The gauche conformation is 3.8 kJ mole^{-1} higher in energy than the anti conformation.



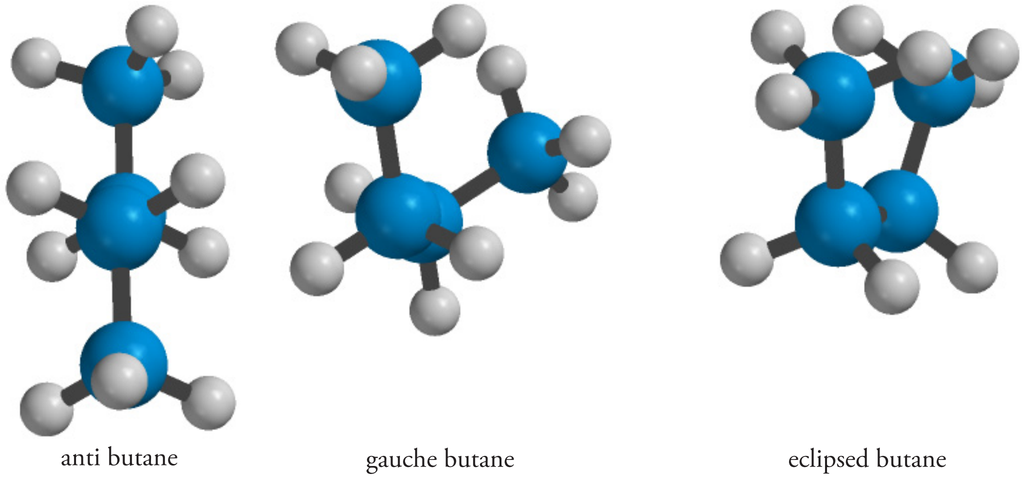


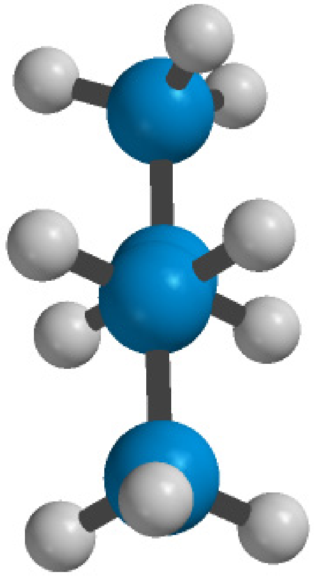
Table 4.4

Energies of Steric Interactions in Alkanes

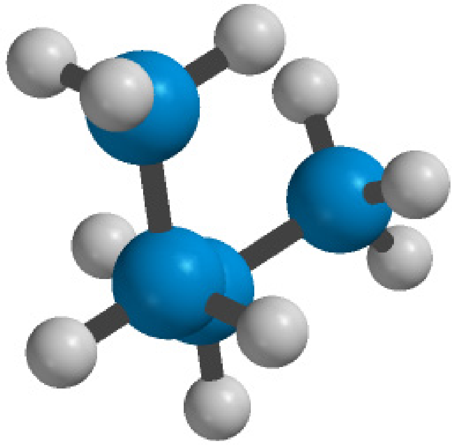
Interaction	Major cause	Energy (kJ mole^{-1})
Eclipsed H/H	torsional	4.2
Eclipsed H/CH_3	torsional	5.4
Eclipsed CH_3/CH_3	torsional + steric	12.6
Gauche CH_3/CH_3	steric	3.8
Gauche H/H (reference)	torsional + steric	0

4.4 CONFORMATIONS OF ALKANES

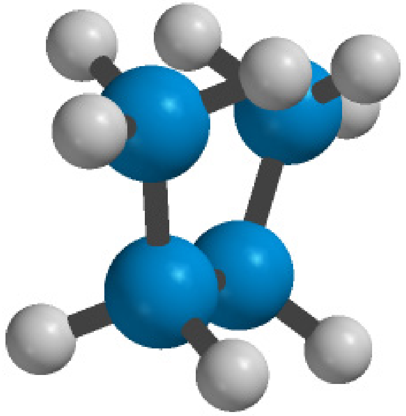
Conformations of Butane



anti butane



gauche butane



eclipsed butane

Table 4.4

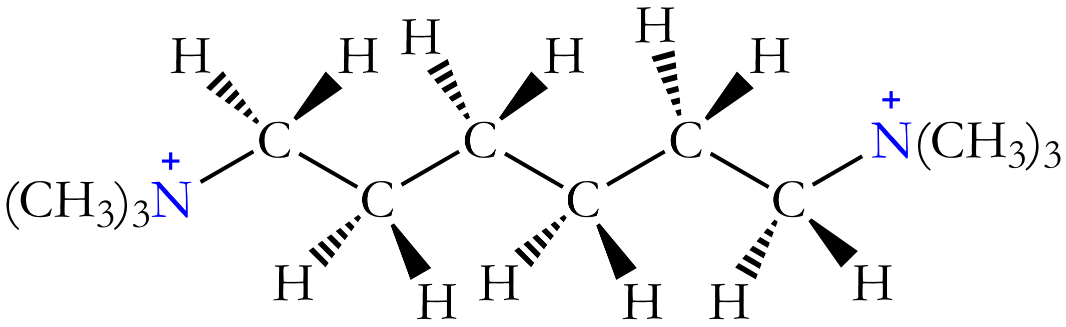
Energies of Steric Interactions in Alkanes

Interaction	**Major cause**	**Energy (kJ mole^{-1})**
Eclipsed H/H	torsional	4.2
Eclipsed H/CH_3	torsional	5.4
Eclipsed CH_3/CH_3	torsional + steric	12.6
Gauche CH_3/CH_3	steric	3.8
Gauche H/H (reference)	torsional + steric	0

4.4 CONFORMATIONS OF ALKANES

Conformations of Acyclic Compounds: Summary

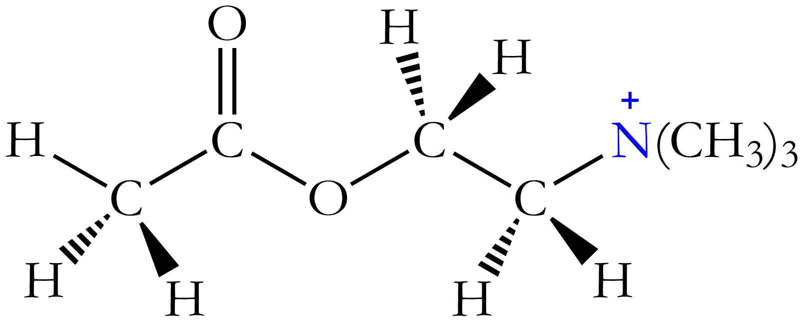
1. The lowest energy conformations have a staggered arrangement for all bonds.
2. Staggered conformations with θ = 180° are more stable that those with θ = 60°.
3. The energy of eclipsing increases in the order hydrogen–hydrogen < hydrogen–alkyl < alkyl–alkyl conformation.



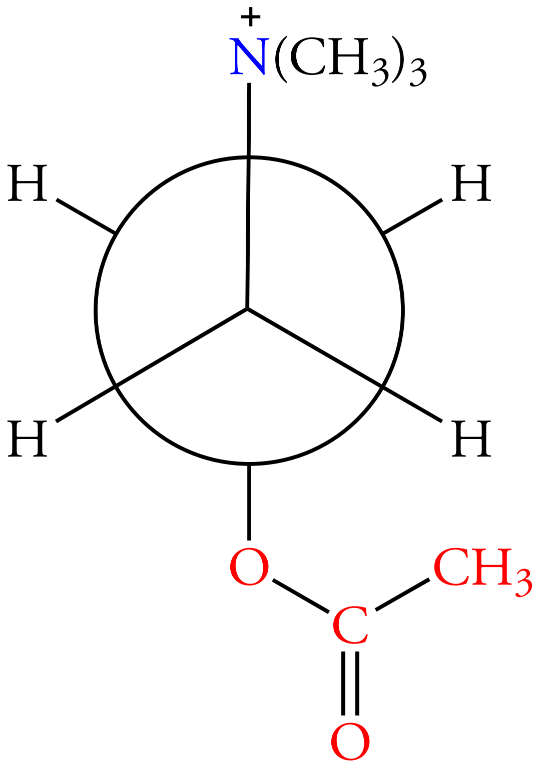
hexamethonium, all anti conformation

4.4 CONFORMATIONS OF ALKANES

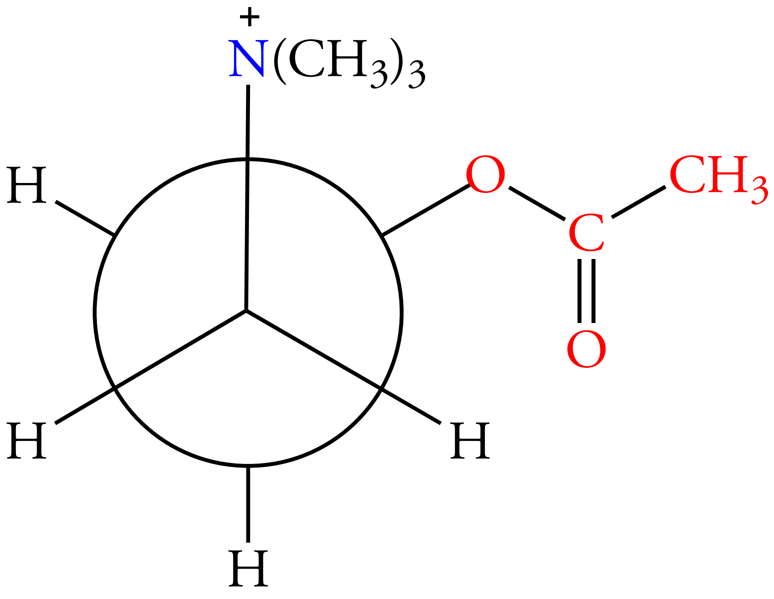
Conformations and Biological Activity



acetyl choline



anti acetylcholine conformation

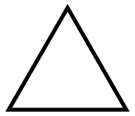


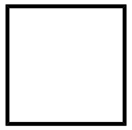
gauche acetylcholine conformation

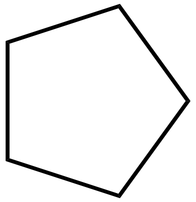
The anti conformation binds nicotinic receptors at ganglia and the acetylcholine receptor at neuromuscular junctions.

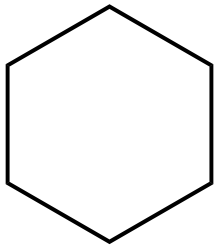
The gauche conformation binds the muscarinic receptor of postganglionic parasympathetic nerves.

4.5 CYCLOALKANES

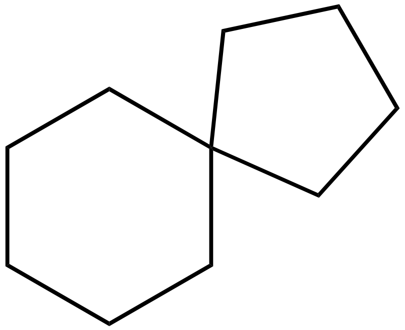

cyclopropane

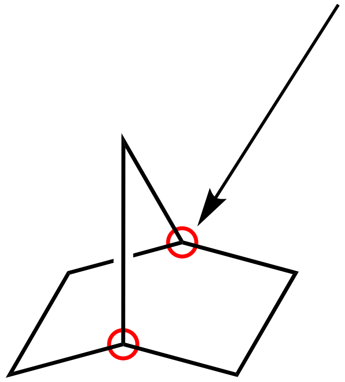

cyclobutane

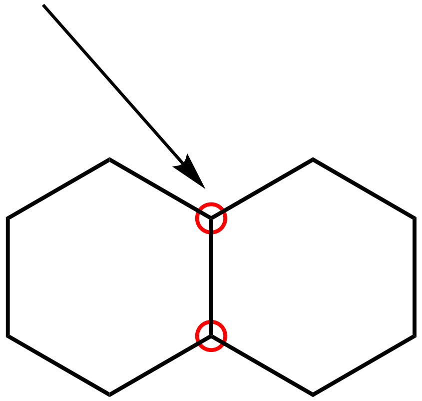

cyclopentane

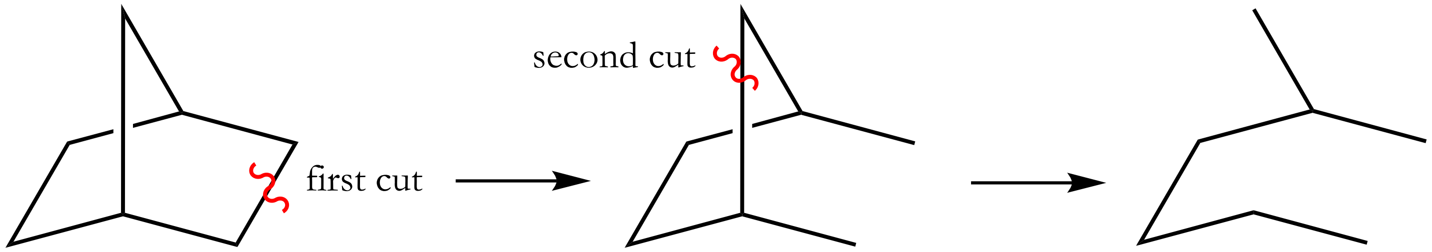

cyclohexane

bridgehead atoms (○)


spirocyclic compound


bicyclic compound

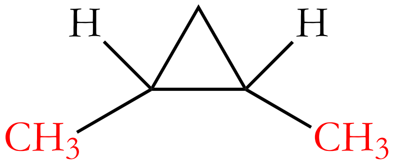

fused-ring compound



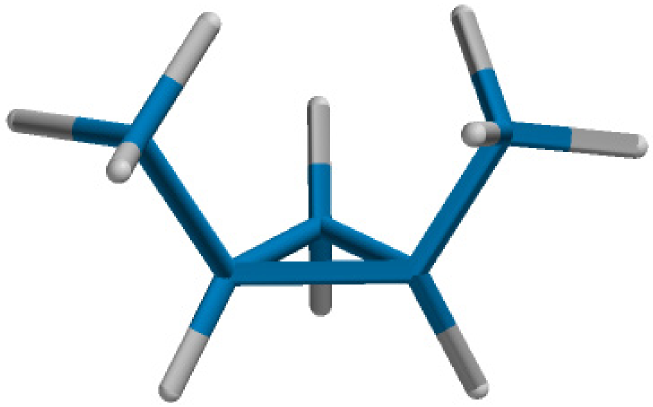
4.4 CONFORMATIONS OF ALKANES

Geometric Isomerism

cis isomer

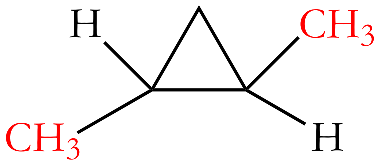


Both methyl groups are on the same side of the plane of the ring atoms.

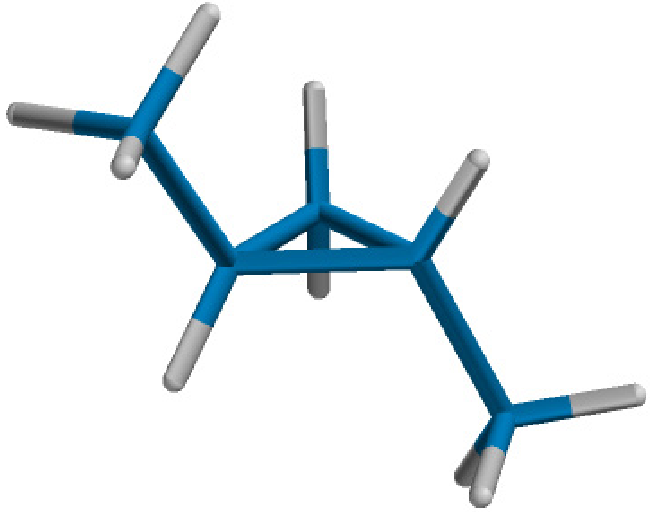


cis-1,2-dimethylcyclopropane

trans isomer

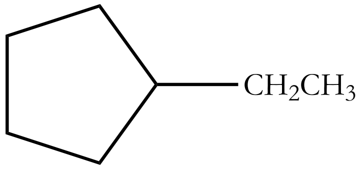


One methyl group is above the plane; the other is below the plane of the ring atoms.

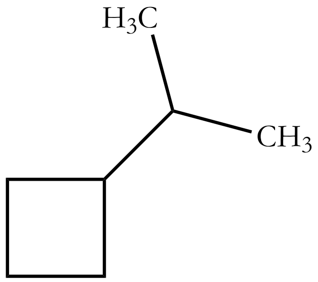


trans-1,2-dimethylcyclopropane

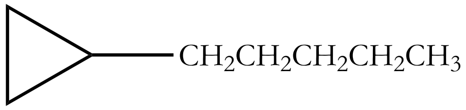
Nomenclature of Cycloalkanes



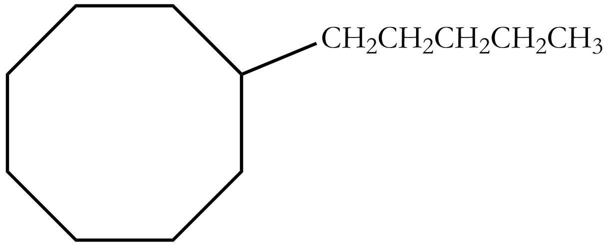
ethylcyclopentane



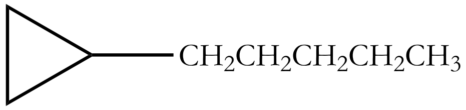
isopropylcyclobutane



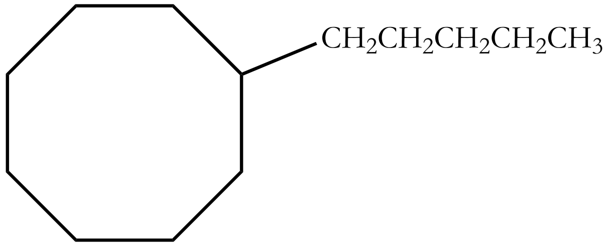
1-cyclopropylpentane



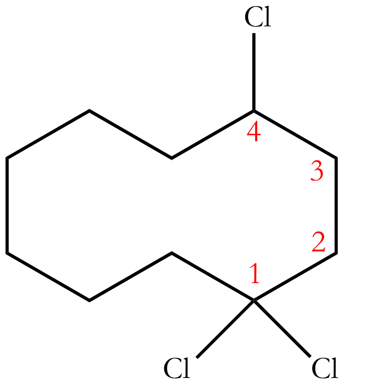
1-pentylcyclooctane



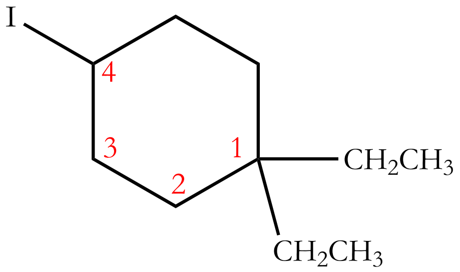
1-cyclopropylpentane



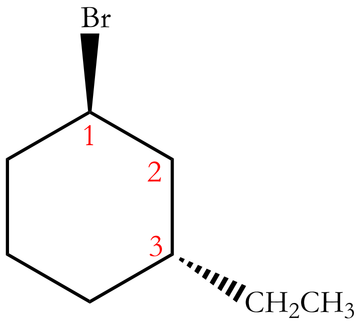
1-pentylcyclooctane



1,1,4-trichlorocyclodecane



1,1-diethyl-4-iodo-cyclohexane



trans-1-bromo-3-ethylcyclohexane

Relative Stabilities of Cycloalkanes

Table 4.5

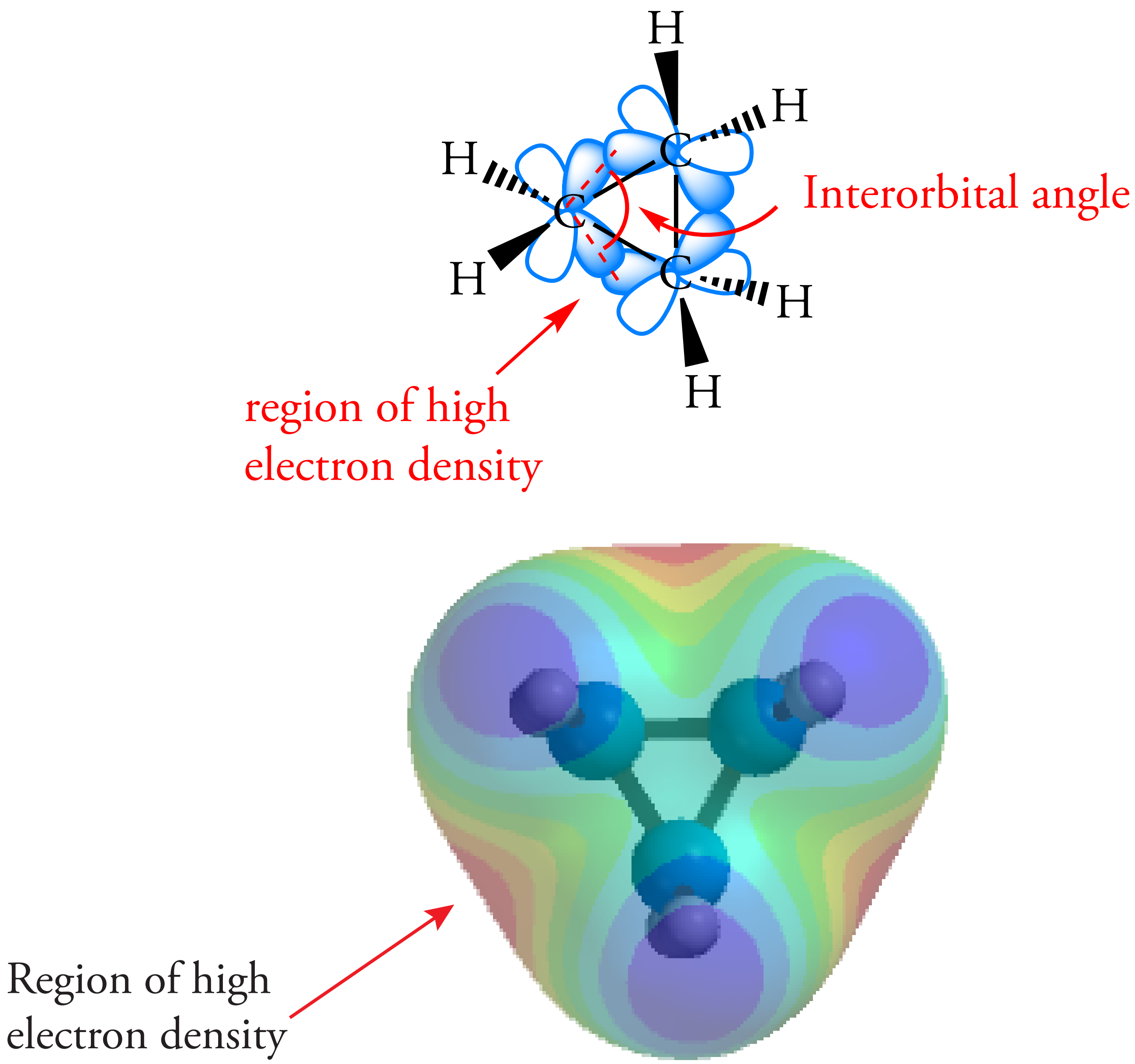
Heats of Formation of Cyclkoalkanes

Cycloalkane	$\Delta H^\circ_{formation}$ kJ mole^{-1}	ΔH°_f (per CH_2 group) kJ mole^{-1}	Strain Energy kJ mole^{-1}
cyclopropane	+53	+17.8	115
cyclobutane	+28.4	+7.1	111
cyclopentane	-77.10	-15.4	26
cyclohexane	-123.19	-20.5	0
cycloheptane	-118.1	-16.9	26
cyclooctane	-124.4	-15.9	40
cyclononane	-132.6	-14.7	53
cyclodecane	-154.3	-15.4	52
alkane (reference)		-20.6	0

$\Delta H^\circ_f - n(20.6 \text{ kJ mole}^{-1})$ = ring strain energy

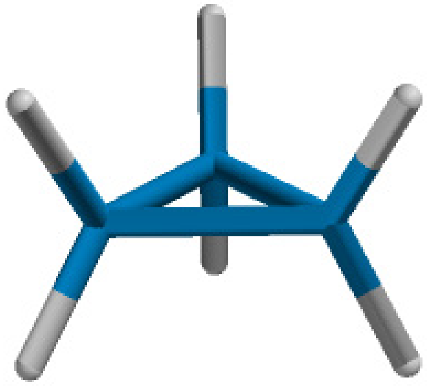
Figure 4.6 Structure and Bonding in Cyclopropane

Cycloalkanes that do not have internuclear angles of 109.5° cannot have efficient overlap of hybrid orbitals. The internuclear bond angle of cyclopropane is 60°, far less than 109.5°. However, the interorbital angle is larger. As a result, the electron density lies “outside” the bond axis and is called a *bent bond*, or sometimes, more whimsically, a banana bond.



4.6 CONFORMATIONS OF CYCLOALKANES

Cyclopropane

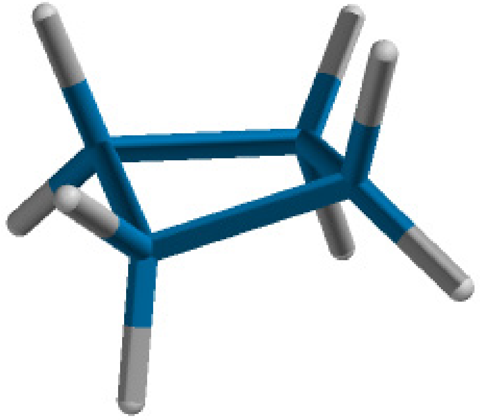


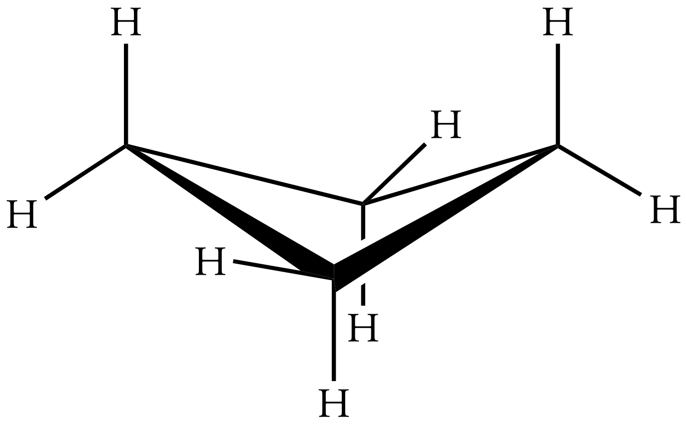
Cyclopropane

Cyclobutane

Figure 4.7 Conformation of Cyclobutane

The conformation of cyclobutane is a slightly bent or twisted ring, which moves the hydrogen atoms away from one another so that they are not completely eclipsed.



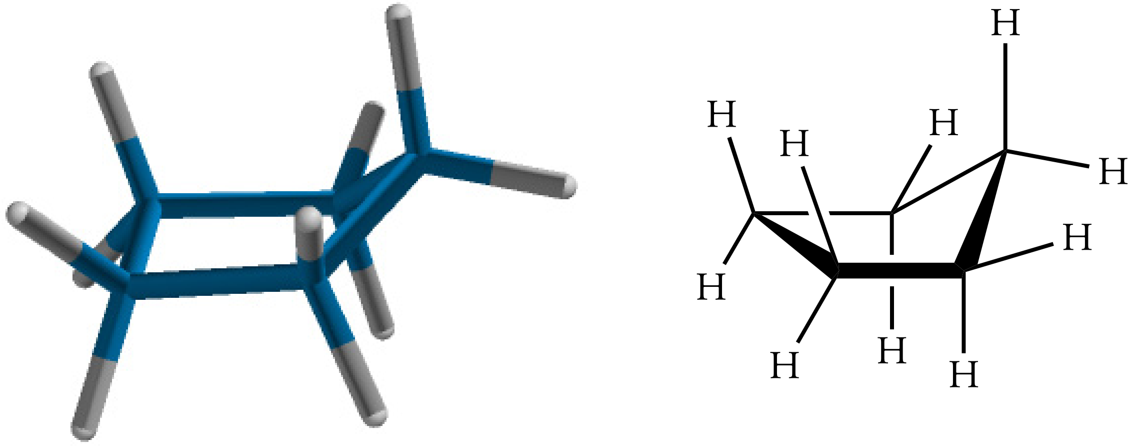


4.6 CONFORMATIONS OF CYCLOALKANES

Cyclopentane

Figure 4.8 Conformations of Cyclopentane

Cyclopentane is a twisted ring in the form of an "envelope," so that one of the carbon atoms is out of the plane of the ring. This decreases the number of eclipsing interactions of hydrogen atoms on adjacent carbons.

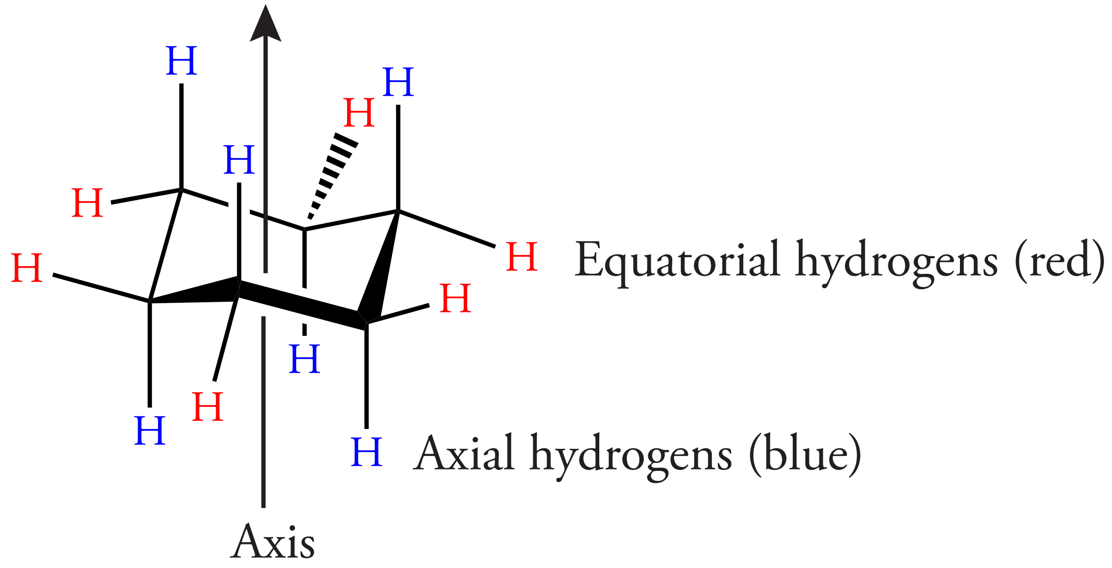


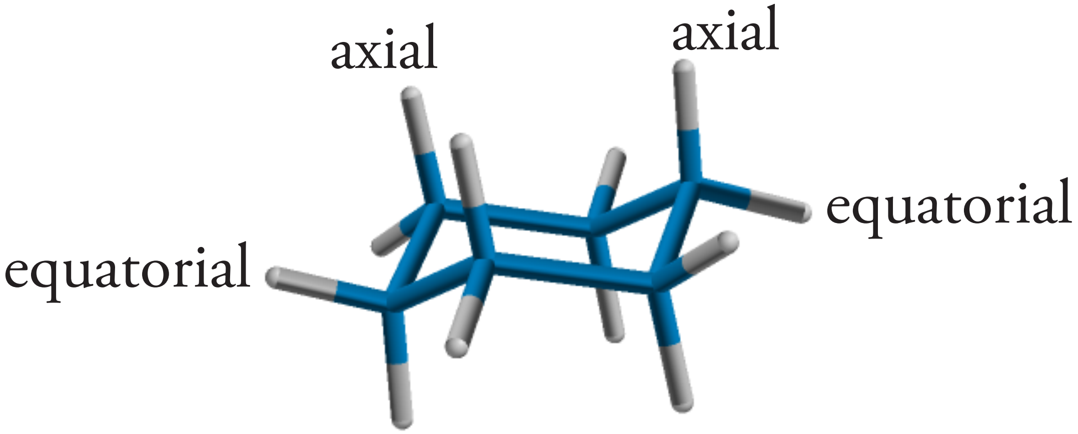
4.6 CONFORMATIONS OF CYCLOALKANES

Cyclohexane

Figure 4.9 Conformations of Cyclohexane

The equatorial C—H bonds lie in a band around the "equator" of the ring. Each carbon atom has one axial hydrogen that is perpendicular to the plane of the ring. The axial hydrogens alternate up and down moving from any axial hydrogen on one carbon to the adjacent carbon.

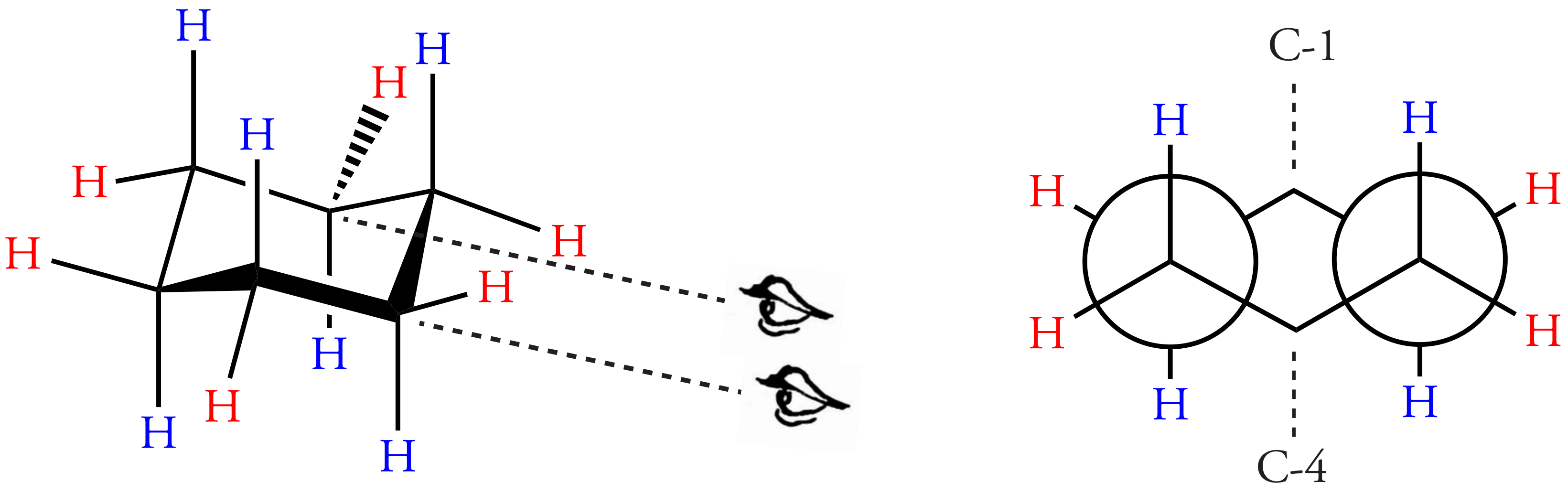




4.6 CONFORMATIONS OF CYCLOALKANES

Figure 4.10 Newman Projection Formula of Cyclohexane

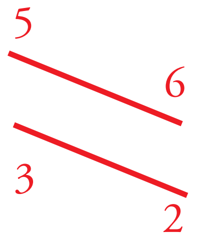
The C-2 to C-3 and C-5 to C-6 bonds of cyclohexane are both viewed and the two ethane-like Newman projections are written side-by-side. The C-1 and C-4 atoms are placed to join the two units, as if they were the pedals of a bicycle.



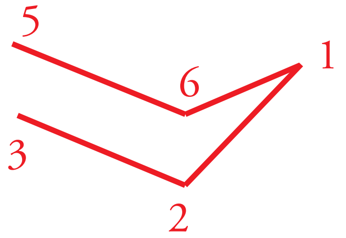
4.6 CONFORMATIONS OF CYCLOALKANES

Drawing Cyclohexane Rings

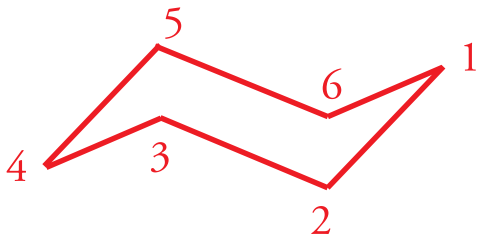
1. Draw one set of parallel lines that slant slightly downward. These are the “seat” of the chair. This orientation matches the chair conformations shown in Figures 4.9 and 4.10. The carbon atoms correspond to bonds from C-2 to C-3 and from C-5 to C-6.



2. Second, place C-1 above and to the right of C-2. Connect C-1 to C-6.

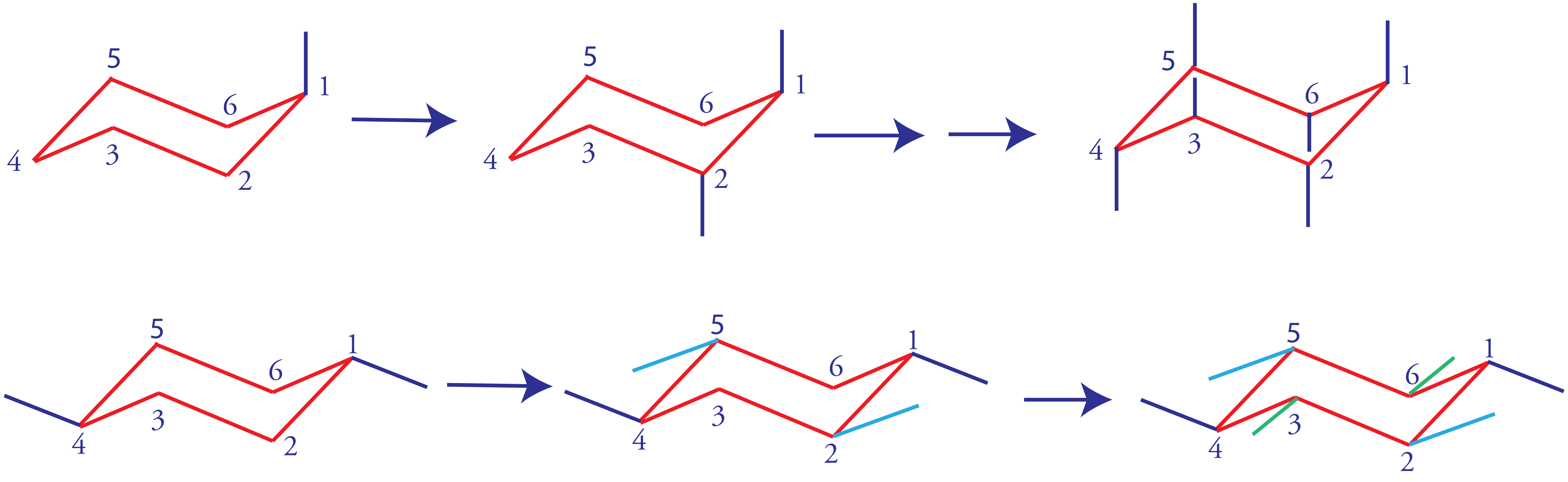


3. Third, place C-4 to the left and below C-3. Then, connect C-3 and C-5 to C-4.



4.6 CONFORMATIONS OF CYCLOALKANES

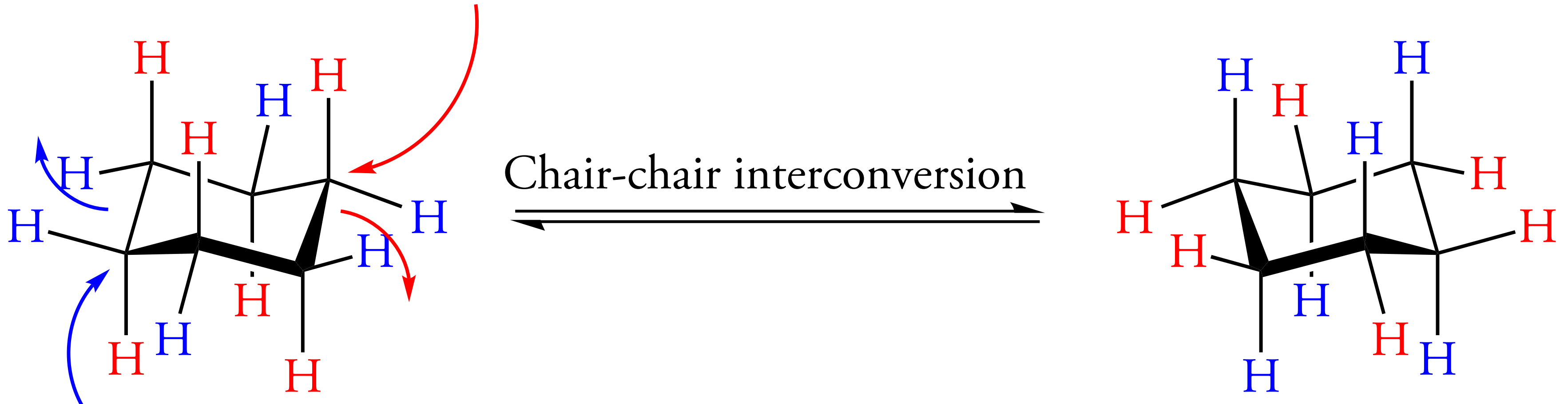
Adding Axial and Equatorial Groups to Cyclohexane Rings



4.7 CONFORMATIONAL MOBILITY OF CYCLOHEXANE

Figure 4.11 Chair-Chair Interconversion of Cyclohexane

The interconversion of two chair conformations of cyclohexane changes all equatorial hydrogens to axial hydrogens, and all axial hydrogens to equatorial hydrogens.



Rotate around bond, top carbon moves down

Chair-chair interconversion

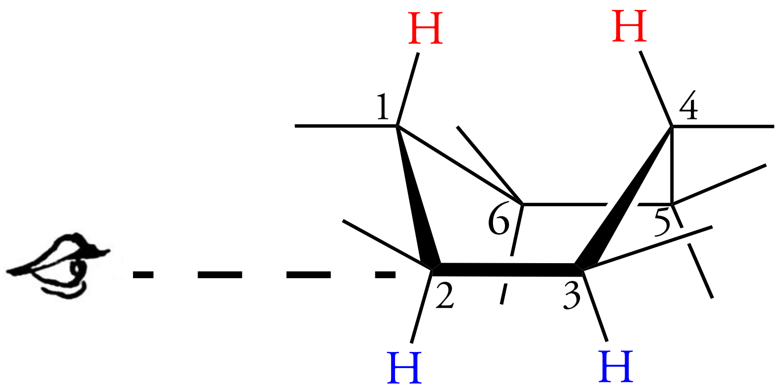
Rotate around bond, bottom carbon moves up

Equatorial hydrogens becomes axial,
axial hydrogens become equatorial.

4.6 CONFORMATIONS OF CYCLOALKANES

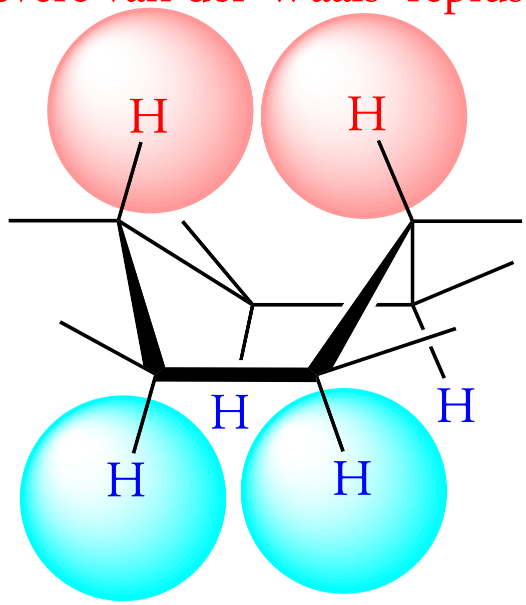
Figure 4.12 Boat Conformation of Cyclohexane

The hydrogens on C-2 to C-3 and C-5 to C-6 bonds of the boat conformation are eclipsed. Also the hydrogens at C-1 and C-4 are so close that their van der Waals radii overlap. As a result, the boat conformation is very unstable.



Hydrogen-hydrogen eclipsing

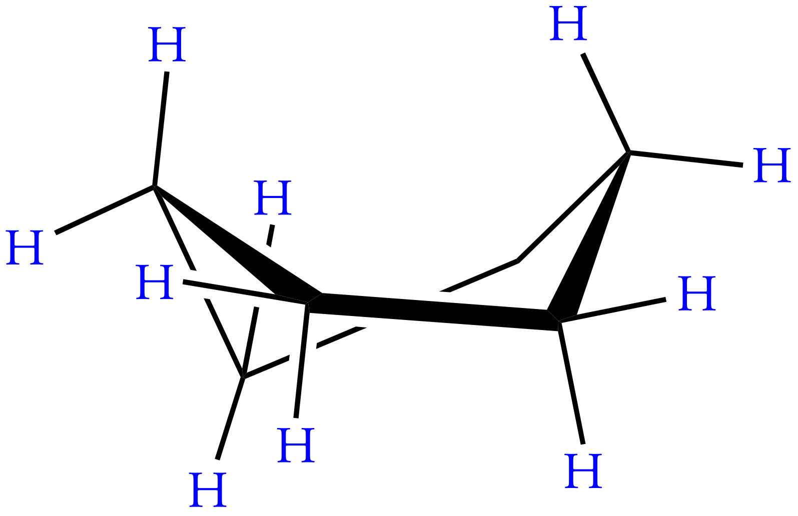
severe van der Waals replusion



Hydrogen-hydrogen eclipsing
(only front pair shown)

4.6 CONFORMATIONS OF CYCLOALKANES

Twist Boat Conformation of Cyclohexane

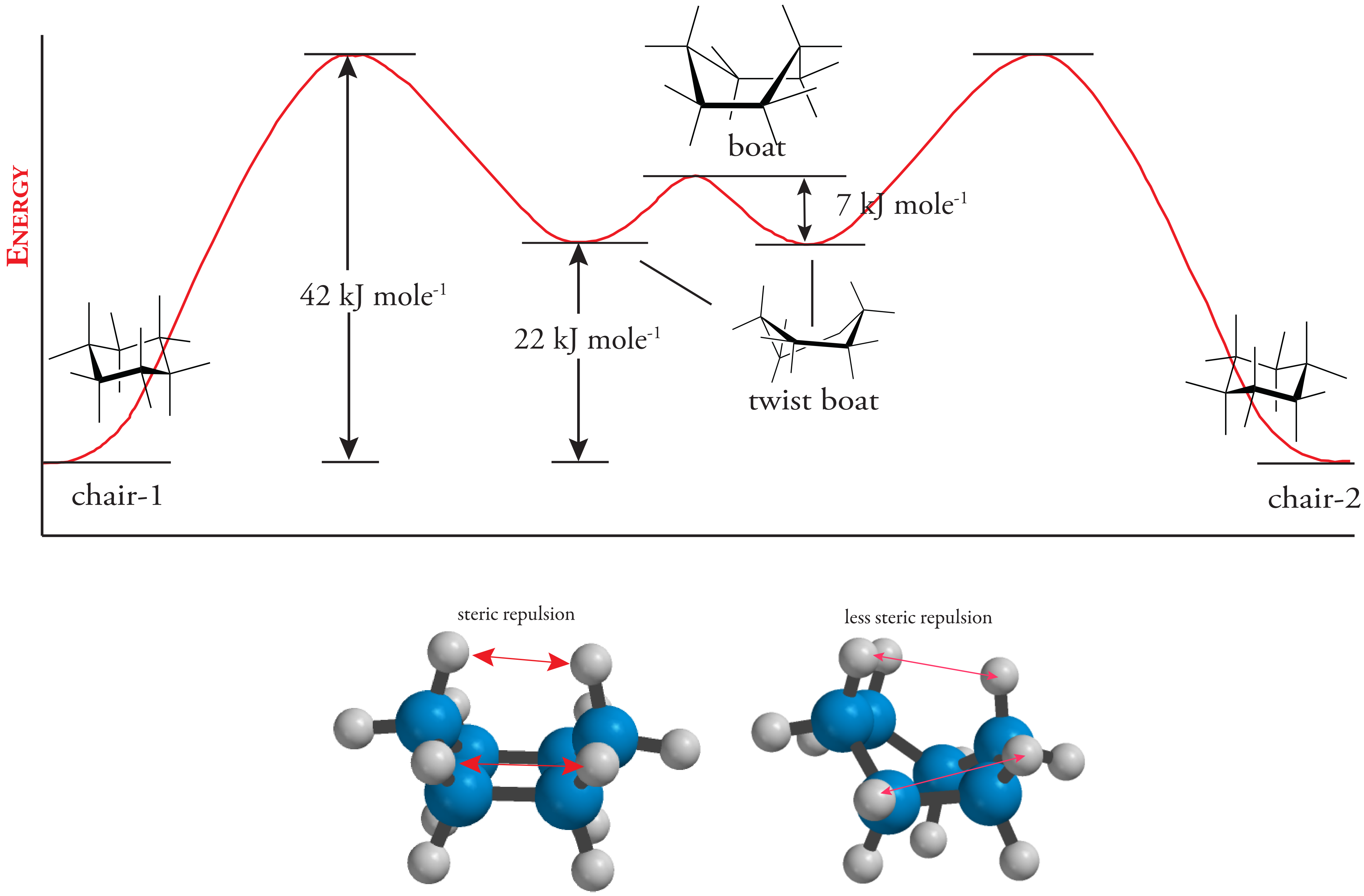


twist boat conformation

4.6 CONFORMATIONS OF CYCLOALKANES

Figure 4.13
Conformational Energies of Cyclohexane

The chair-chair interconversion of cyclohexane passes through twist boat conformations that are in equilibrium with a boat conformation.



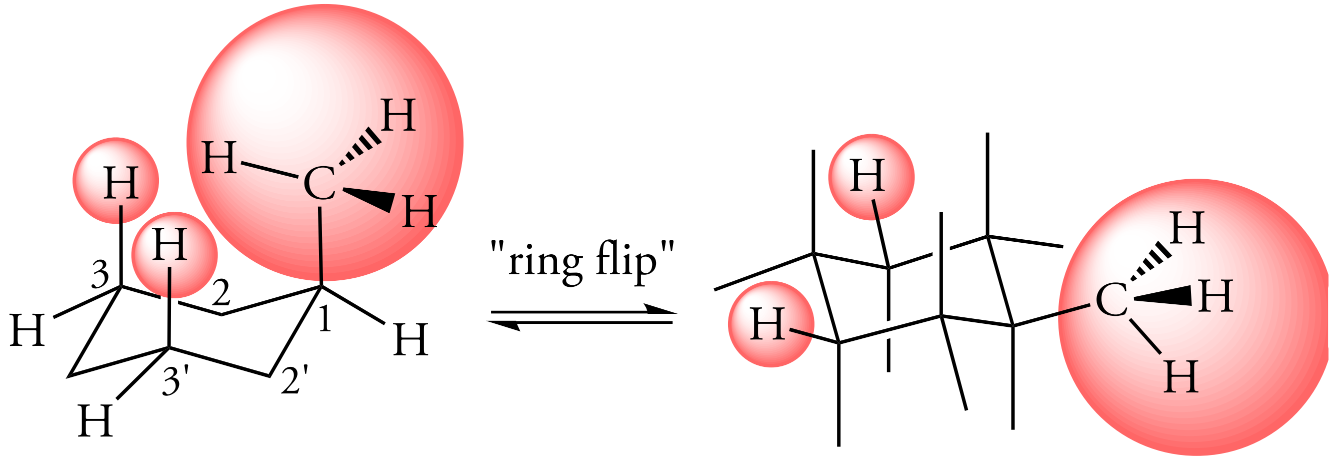
boat conformation

twist boat conformation

4.8 MONOSUBSTITUTED CYCLOHEXANES

Figure 4.14 Conformations of Methyl Cyclohexane

Methylcyclohexane rapidly interconverts between two conformations of unequal energy. At room temperature, 95% of the conformations have an equatorial methyl group, and 5% have an axial methyl group. The axial conformation has unfavorable interactions with axial hydrogens at C-3 and C-3'.

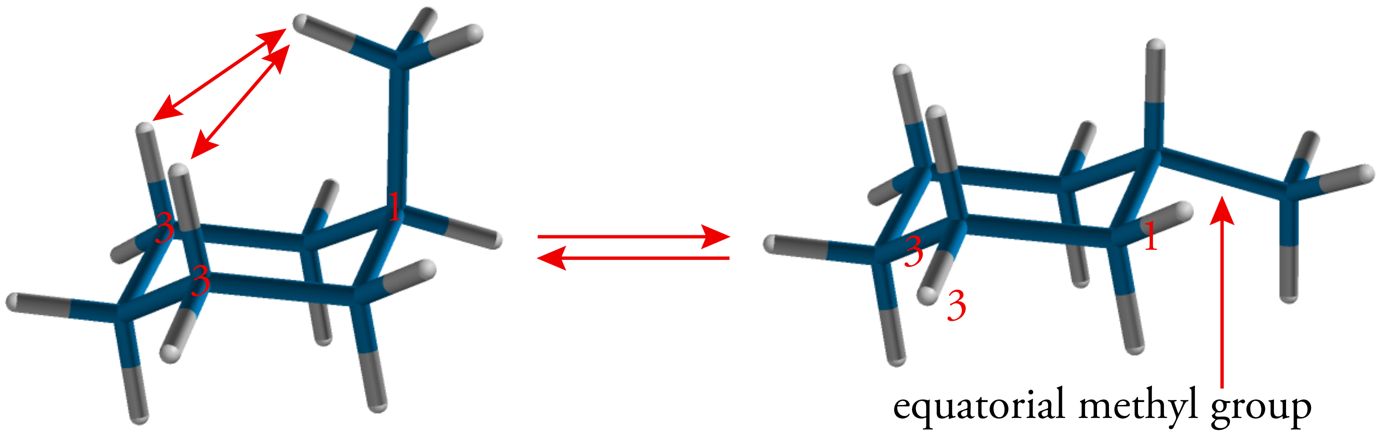


methylcyclohexane
(axial methyl group)

methylcyclohexane
(equatorial methyl group)

two 1,3-diaxial interactions

no 1,3-diaxial interactions, more stable



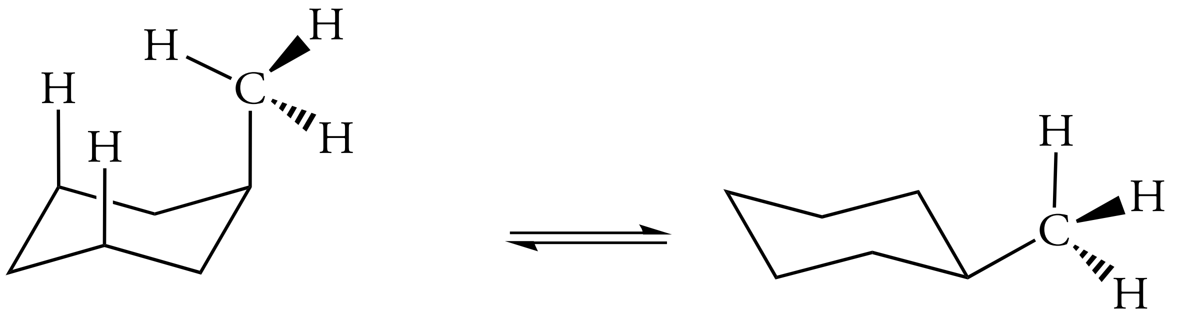
equatorial methyl group

4.6 CONFORMATIONS OF CYCLOALKANES

Table 4.6

Conformational Preferences of Groups

Group	Strain energy (kJ mole^{-1})
CN	0.8
F	1.0
Cl	2.8
OH	4.2
CH_3	7.6
CH_3—CH_2	8.0
$(CH_3)_2CH$	9.2
$(CH_3)_3C$	22
CO_2H	5.8



two 1,3-diaxial interactions
5%

no 1,3-diaxial interactions
95%

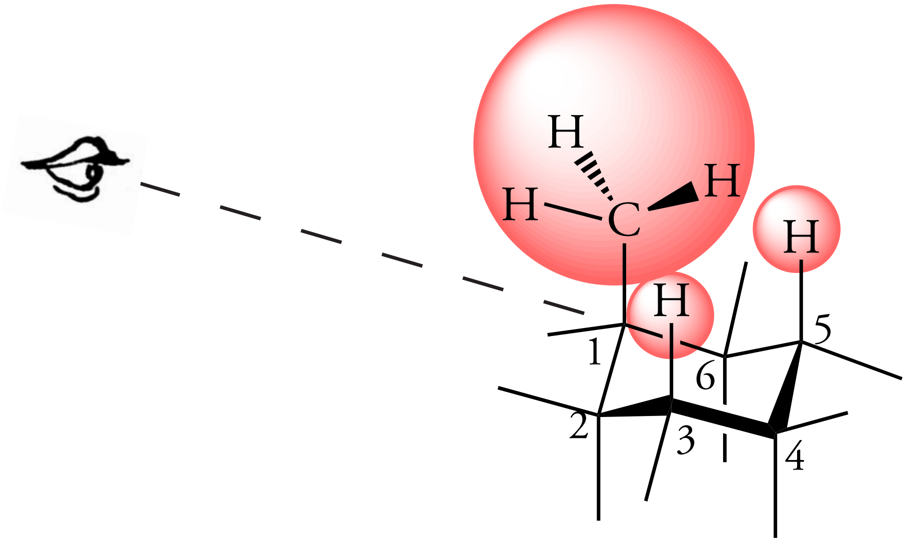
4.6 CONFORMATIONS OF CYCLOALKANES

Figure 4.15 1,3-Diaxial Interactions in Methylcyclohexane

An axial methyl group is at a 60° dihedral angle with respect to the methylene groups at C-3 and C-5. this interaction is equivalent to two gauche butane interactions. Sighting down the C-1 to C-6 bond shows the eclipsing of the methyl group by the C-5 axial hydrogen atom.

two identical 1-3-diaxial interactions, equivalent to gauche butane

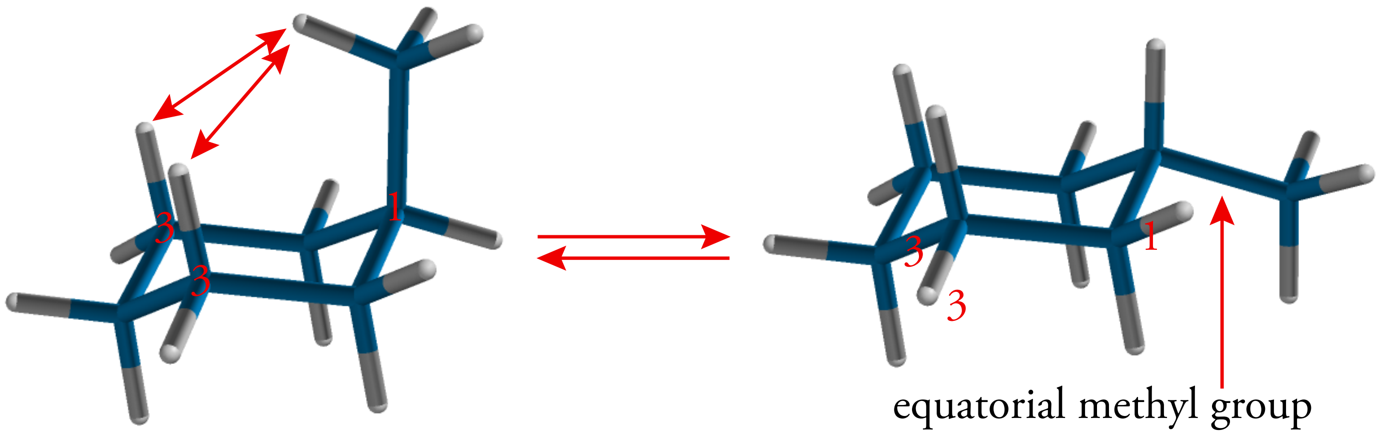
Look along the C-1 to C-6 bond to see the eclipsed, gauche butane interaction.



methylcyclohexane
(axial conformation)

two 1,3-diaxial interactions

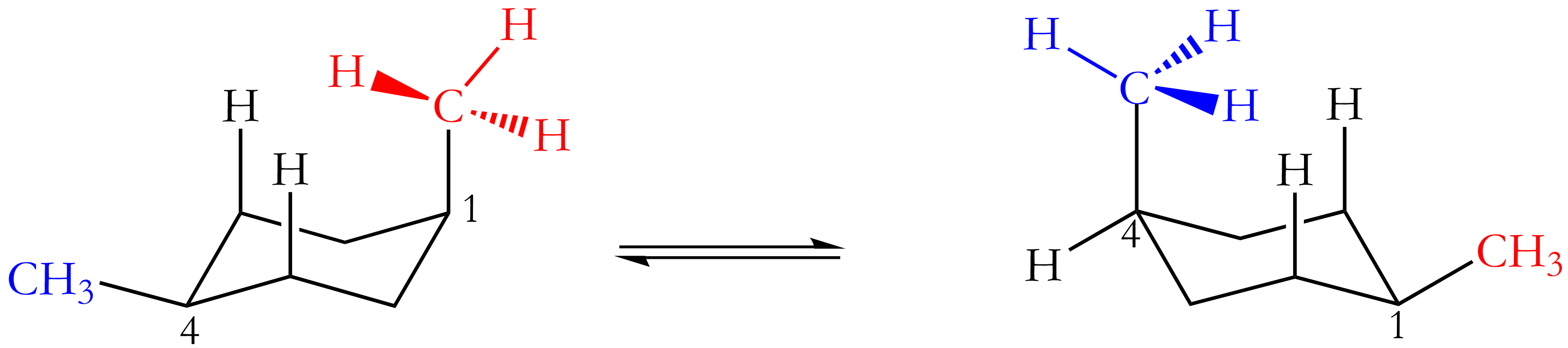
no 1,3-diaxial interactions, more stable



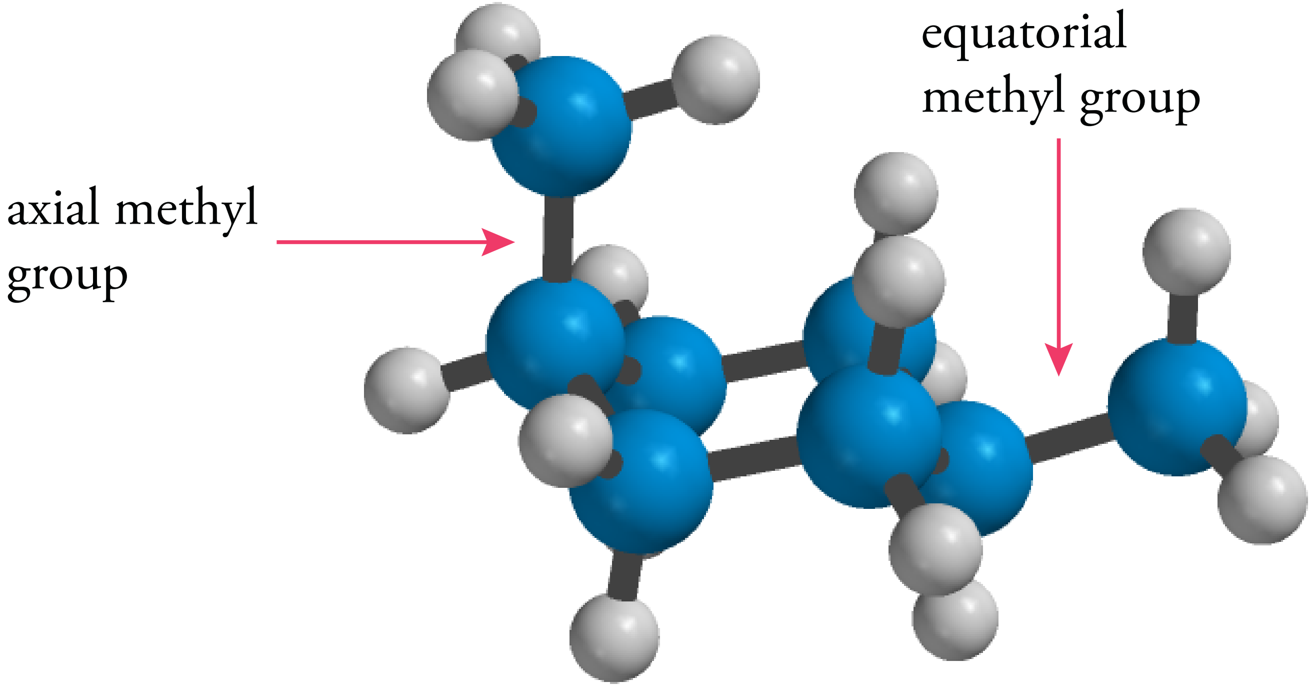
equatorial methyl group

4.9 DISUBSTITUTED CYCLOHEXANES

cis-1,4-Dimethylcyclohexane



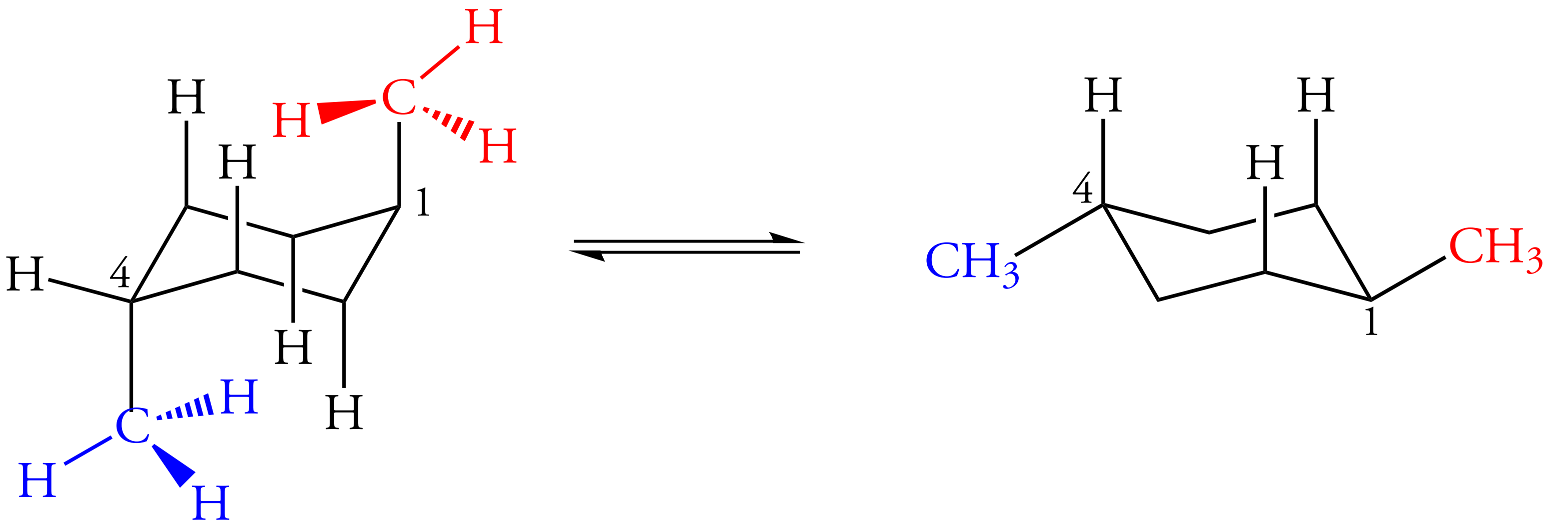
cis-1,4-dimethylcyclohexane



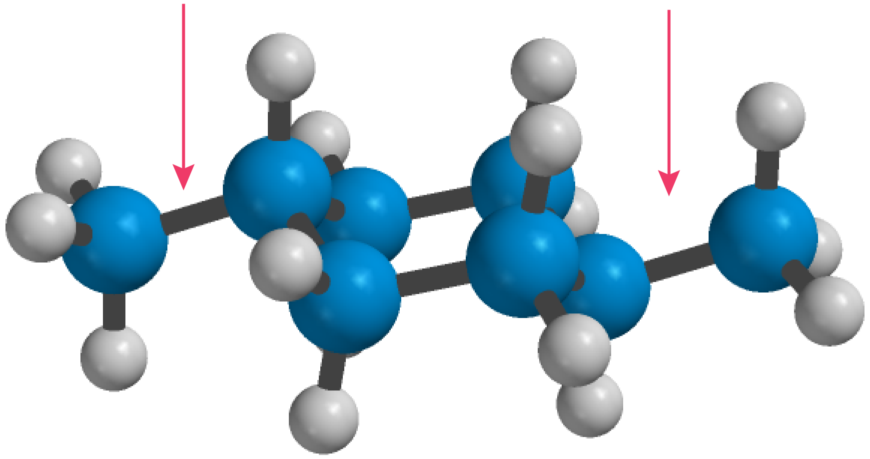
cis-1,4-dimethylcyclohexane

4.9 DISUBSTITUTED CYCLOHEXANES

trans-1,4-Dimethylcyclohexane



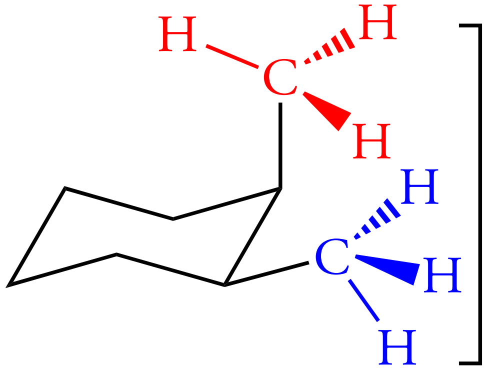
trans-1,4-dimethylcyclohexane


equatorial methyl groups

trans-1,4-dimethylcyclohexane

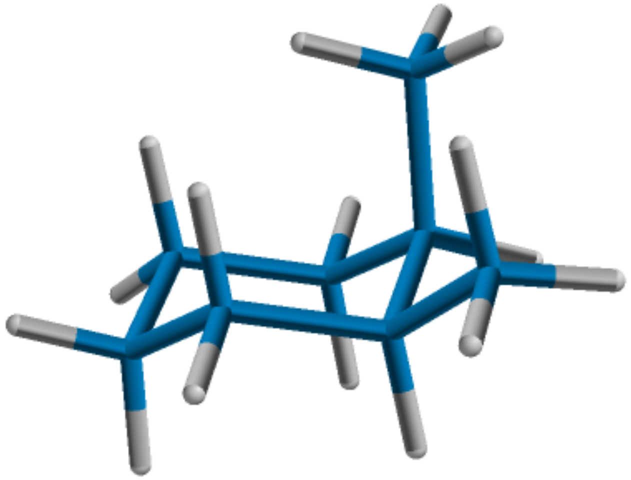
4.9 DISUBSTITUTED CYCLOHEXANES

cis-1,2-Dimethylcyclohexane

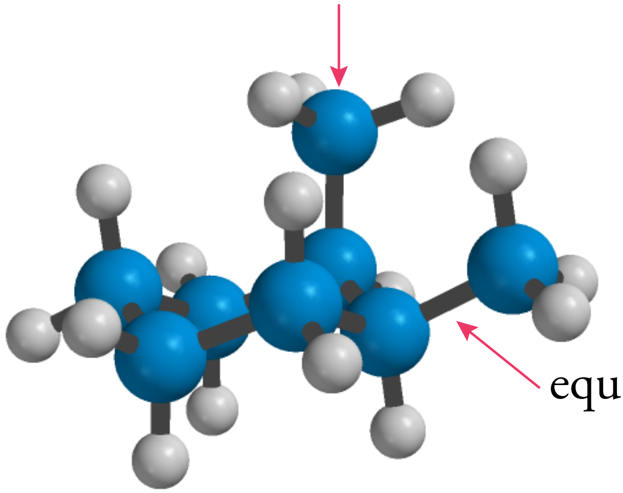


gauche butane interaction

cis-1,2-dimethylcyclohexane



axial methyl group

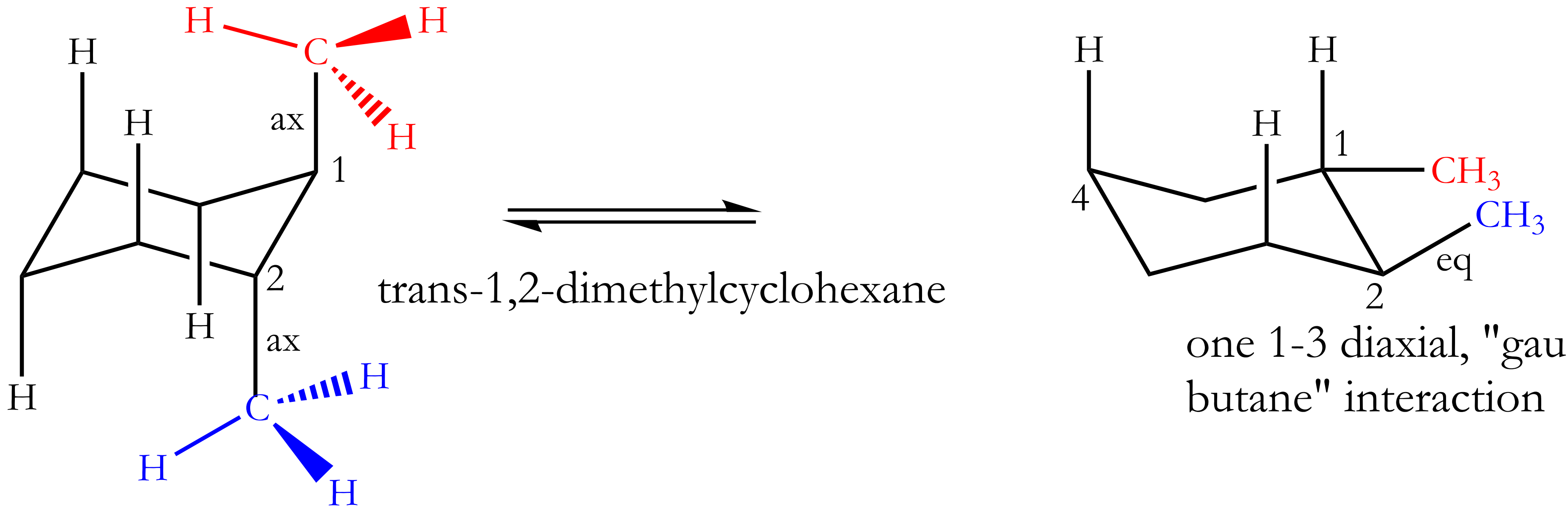


equatorial methyl group

cis-1,2-dimethylcyclohexane

4.9 DISUBSTITUTED CYCLOHEXANES

trans-1,2-Dimethylcyclohexane

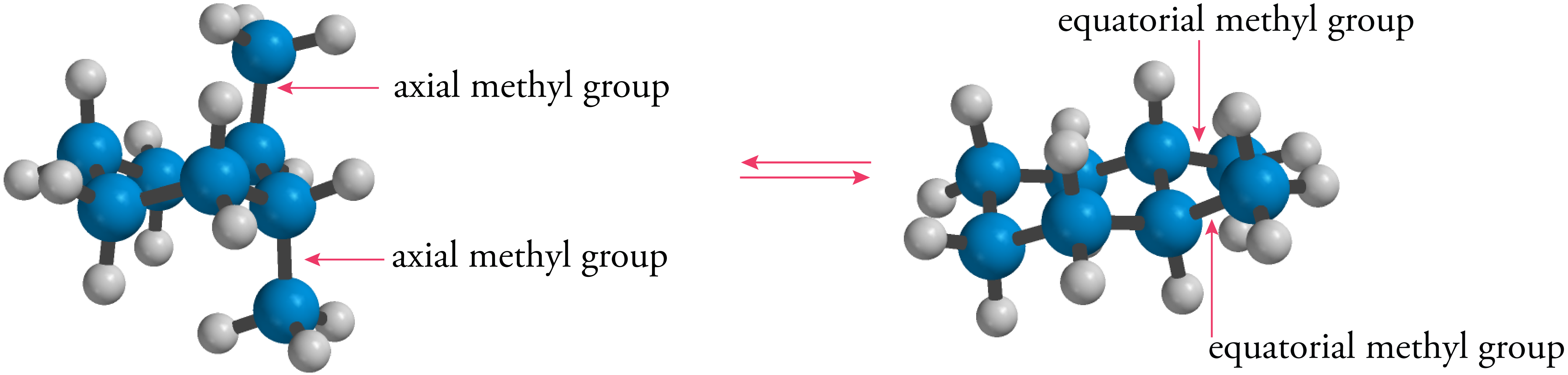


two 1-3 diaxial, "gauche butane" interactions

trans-1,2-dimethylcyclohexane

one 1-3 diaxial, "gauche butane" interaction

two 1-3 diaxial, "gauche butane" interactions



axial methyl group

axial methyl group

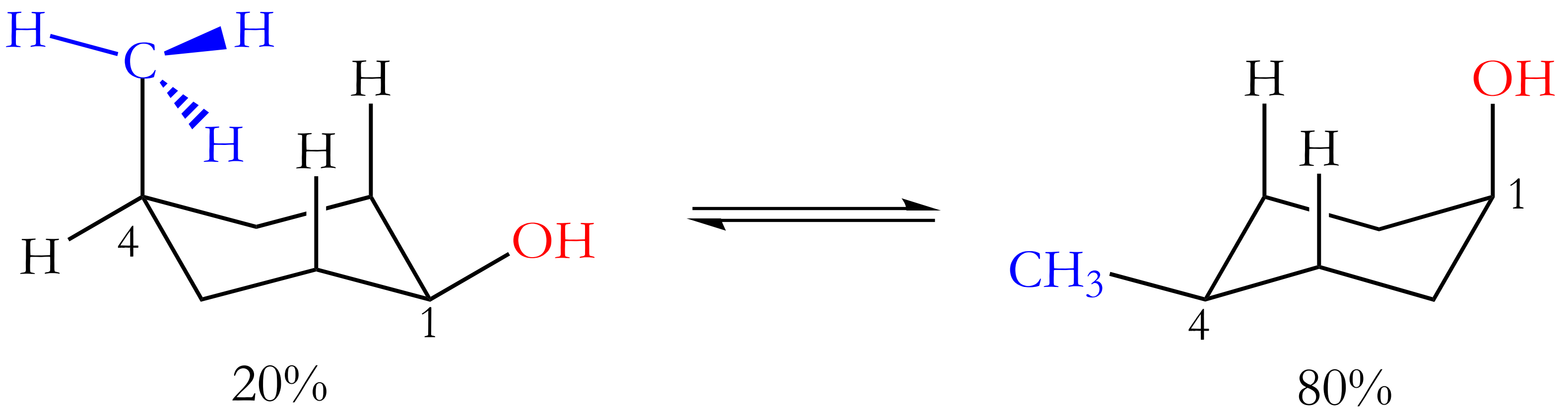
equatorial methyl group

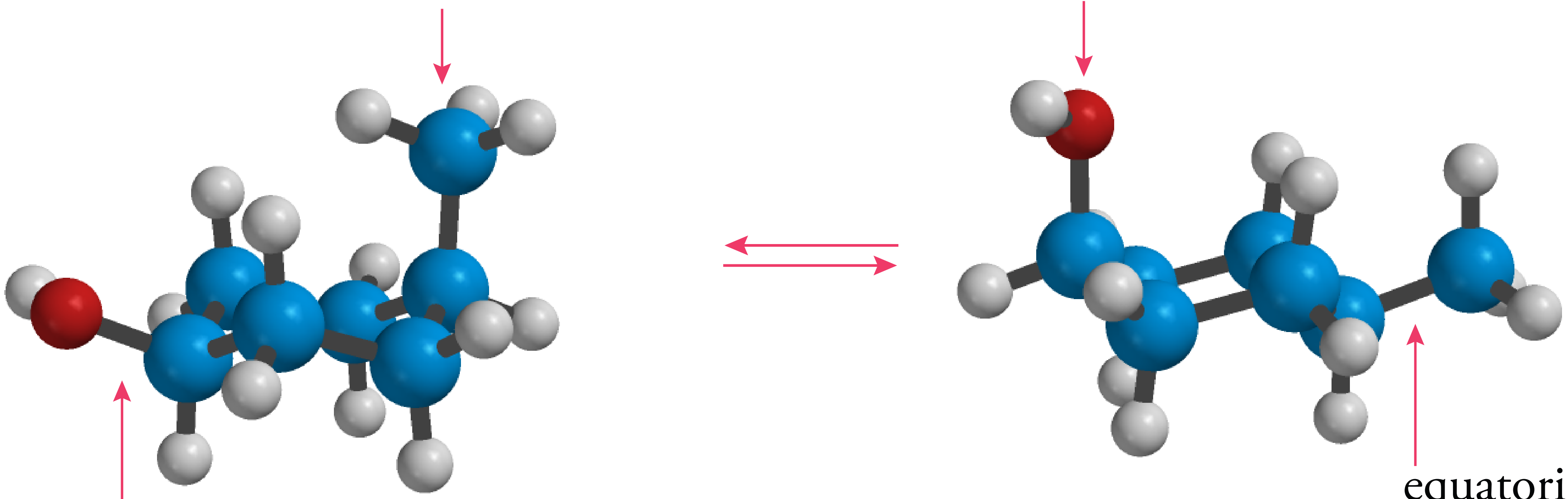
equatorial methyl group

trans-1,2-dimethylcyclohexane

4.9 DISUBSTITUTED CYCLOHEXANES

Compounds with Two Different Substituents: cis-4-methylcyclohexanol




axial methyl group

axial hydroxyl group

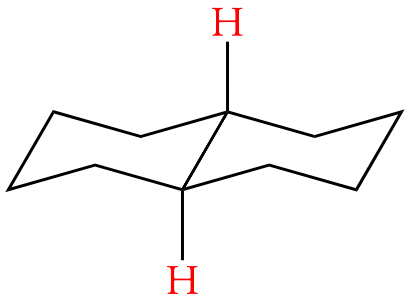
equatorial hydroxyl group

equatorial
methyl group

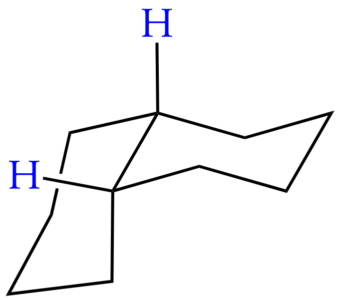
Conformations of *cis*-4-methylcyclohexanol

4.10 POLYCYCLIC MOLECULES

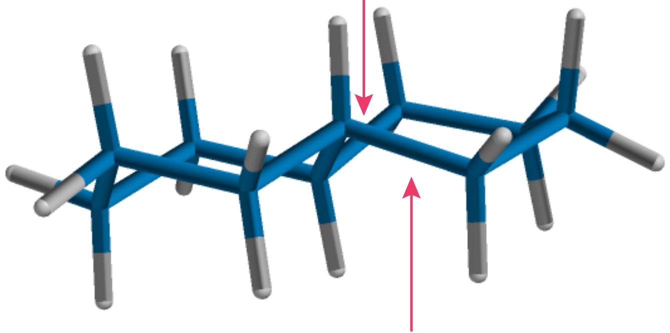
cis- and trans-Decalin



trans-decalin



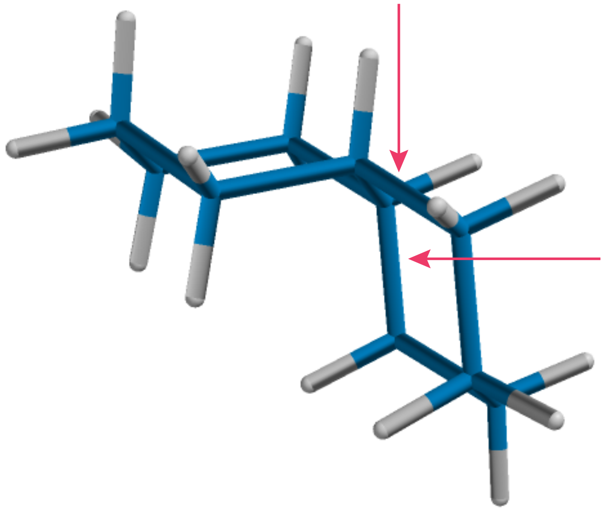
cis-decalin



equatorial CH_2 group

equatorial CH_2 group

trans-decalin



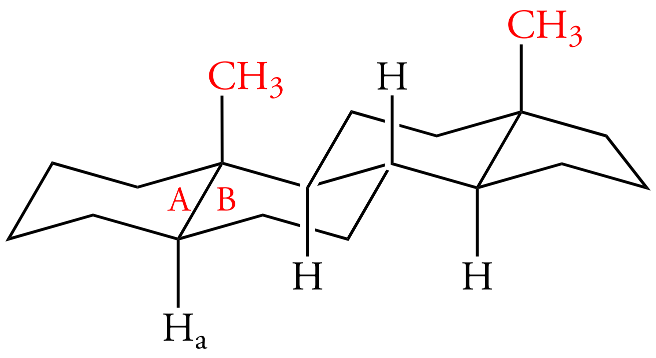
equatorial CH_2 group

axial CH_2 group

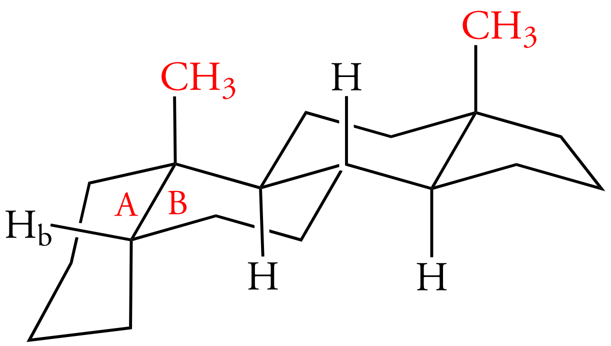
cis-decalin

4.10 POLYCYCLIC MOLECULES

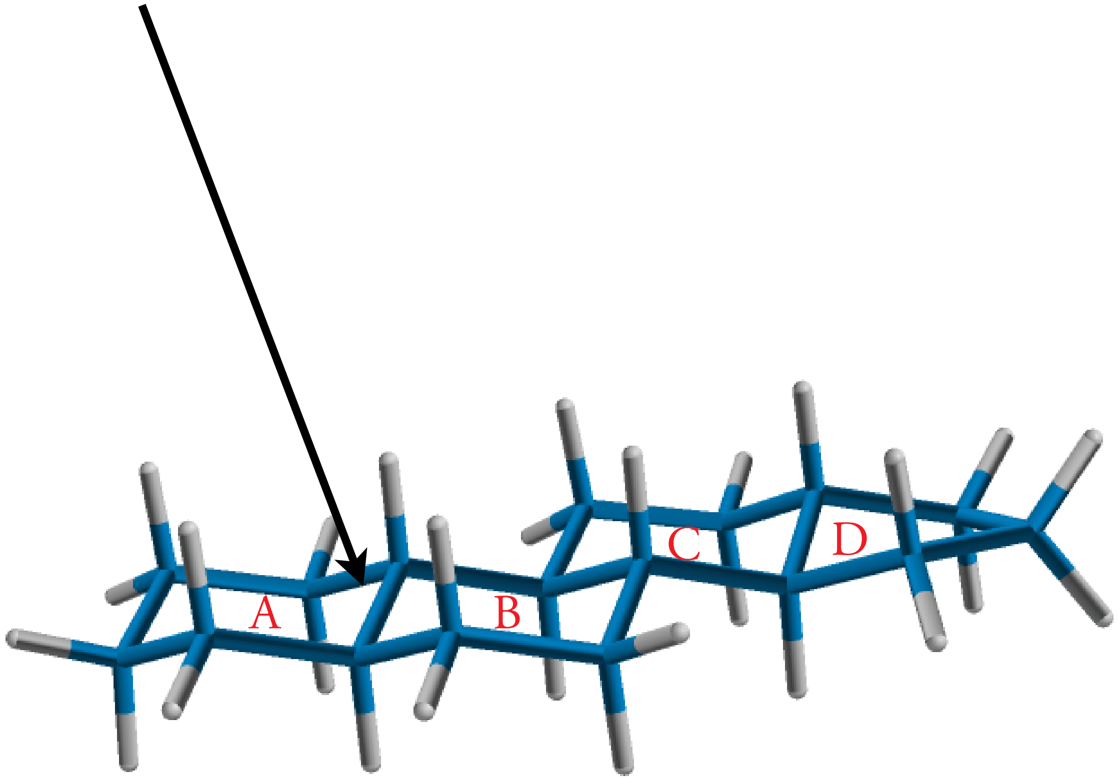
The Steroid Ring System



trans (A/B) ring junction



cis (A/B) ring junction

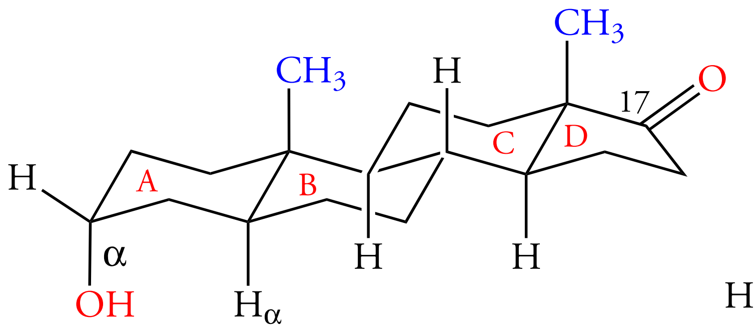


Conformation of the steroid ring system

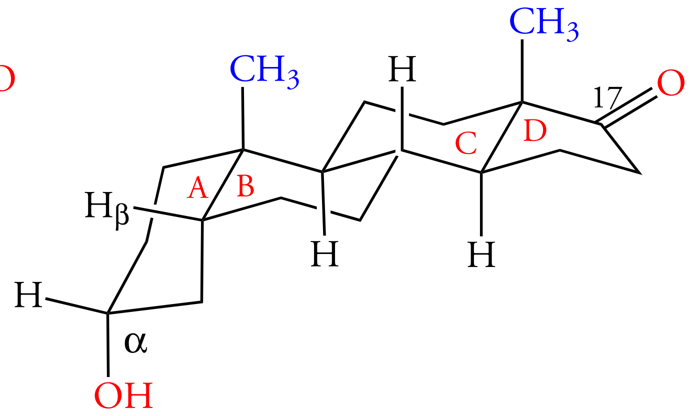
4.10 POLYCYCLIC MOLECULES

Human Physiological Effects of Steroids

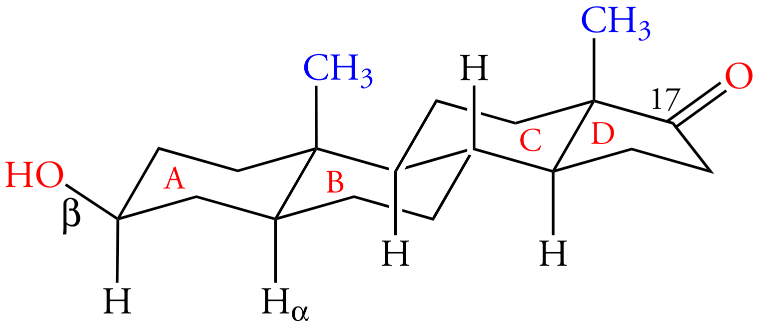
Figure 4.16 Structure and Androgen Activity



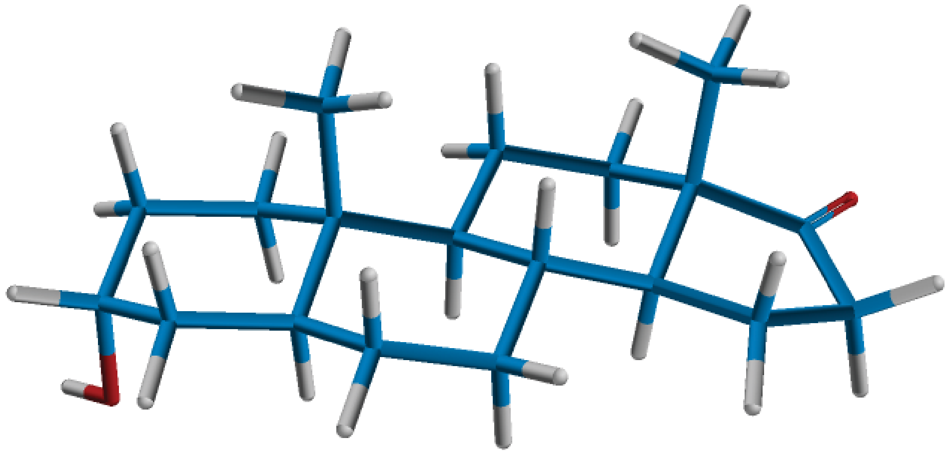
androsterone (high activity)



5-β-androsterone (no activity)



epiandrosterone (reduced activity)



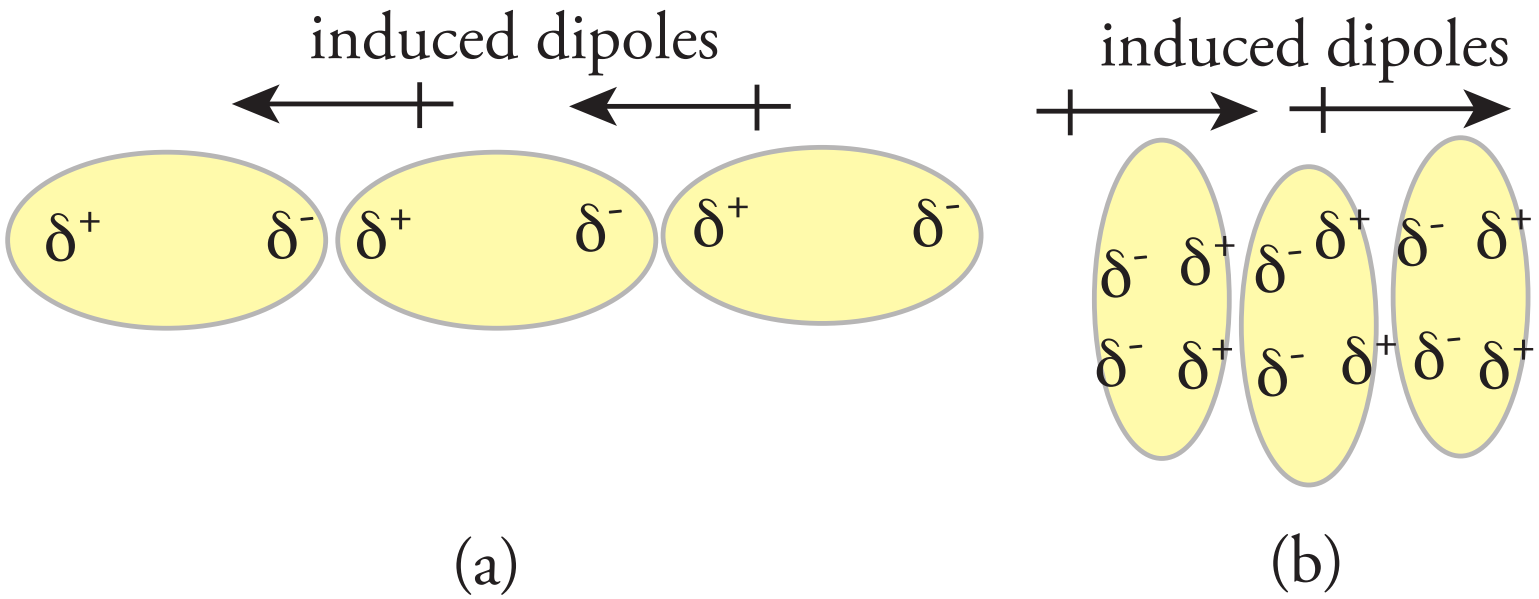
Androsterone

4.11 PHYSICAL PROPERTIES OF ALKANES

van der Waals Forces (London Forces)

Figure 4.17 van der Waals Forces

(a) The approach of one nonpolar molecule induces a transient dipole in its neighbor "end-to-end". (b) Several nonpolar molecules interacting side-by-side by van der Walls interactions.



4.11 PHYSICAL PROPERTIES OF ALKANES

Boiling Points of Alkanes

$CH_3CH_2CH_2CH_2CH3$

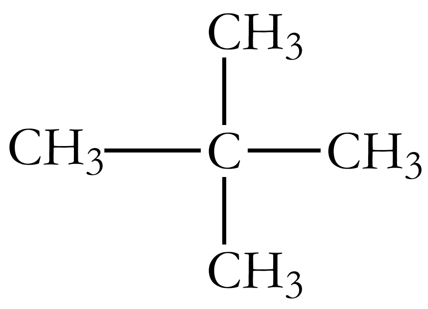
pentane

b.p. 36 °C

$CH_3CH_2CH_2CH_2CH_2CH_3$

hexane

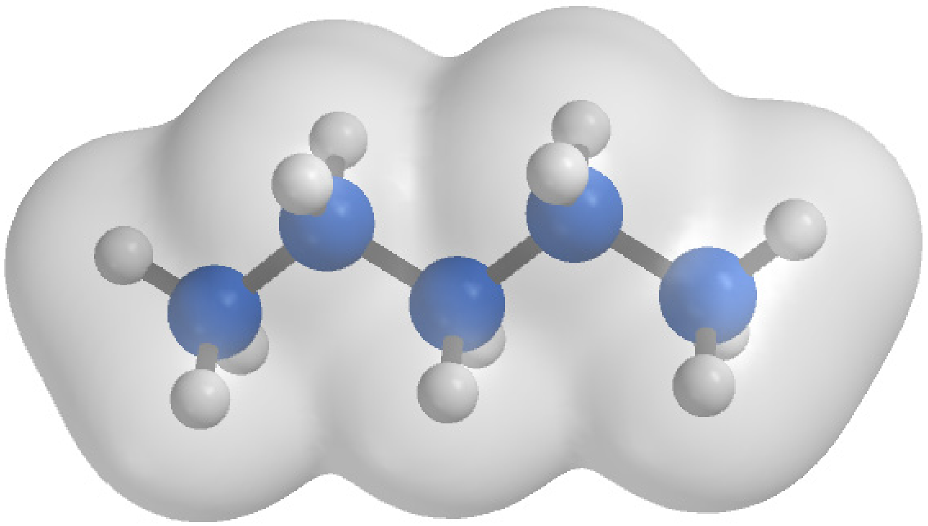
b.p. 69 °C



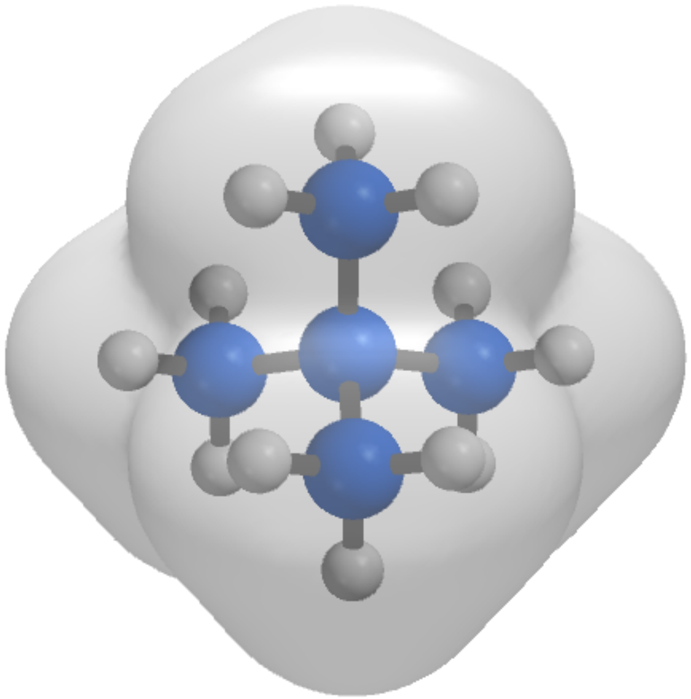
$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array}$$

neopentane

bp -10 °C



n-pentane



neopentane

4.11 PHYSICAL PROPERTIES OF ALKANES

Densities of Alkanes

Table 4.7

Physical Properties of Some Alkanes and Cycloalkanes

Hydrocarbon	Boiling Point (°C)	Density g/mL
methane	-164.0	0.678
ethane	-88.6	0.691
propane	42.1	0.690
butane	-0.5	0.711
pentane	36.1	0.6262
hexane	68.9	0.6603
heptane	98.4	0.6837
octane	125.7	0.7025
decane	150.8	0.7176
cyclopropane	-32.7	(gas at 20 °C)
cyclobutane	12	(gas at 20 °C)
cyclopentane	49.3	0.7457
cyclohexane	80.7	0.7786
cycloheptane	110.5	0.8098
cyclooctane	148.5	0.8349

4.12 STABILITIES OF ALKYL RADICALS

Bond Dissociation Energies of Alkanes

$$CH_3\text{—}H \longrightarrow CH_3\cdot \quad + \quad \cdot H \qquad \Delta H^\circ = 438 \text{ kJ mole}^{-1}$$

CH_3—H > primary C—H > secondary C—H > tertiary C —H

Table 4.8
Bond Dissociation Energies of Alkanes

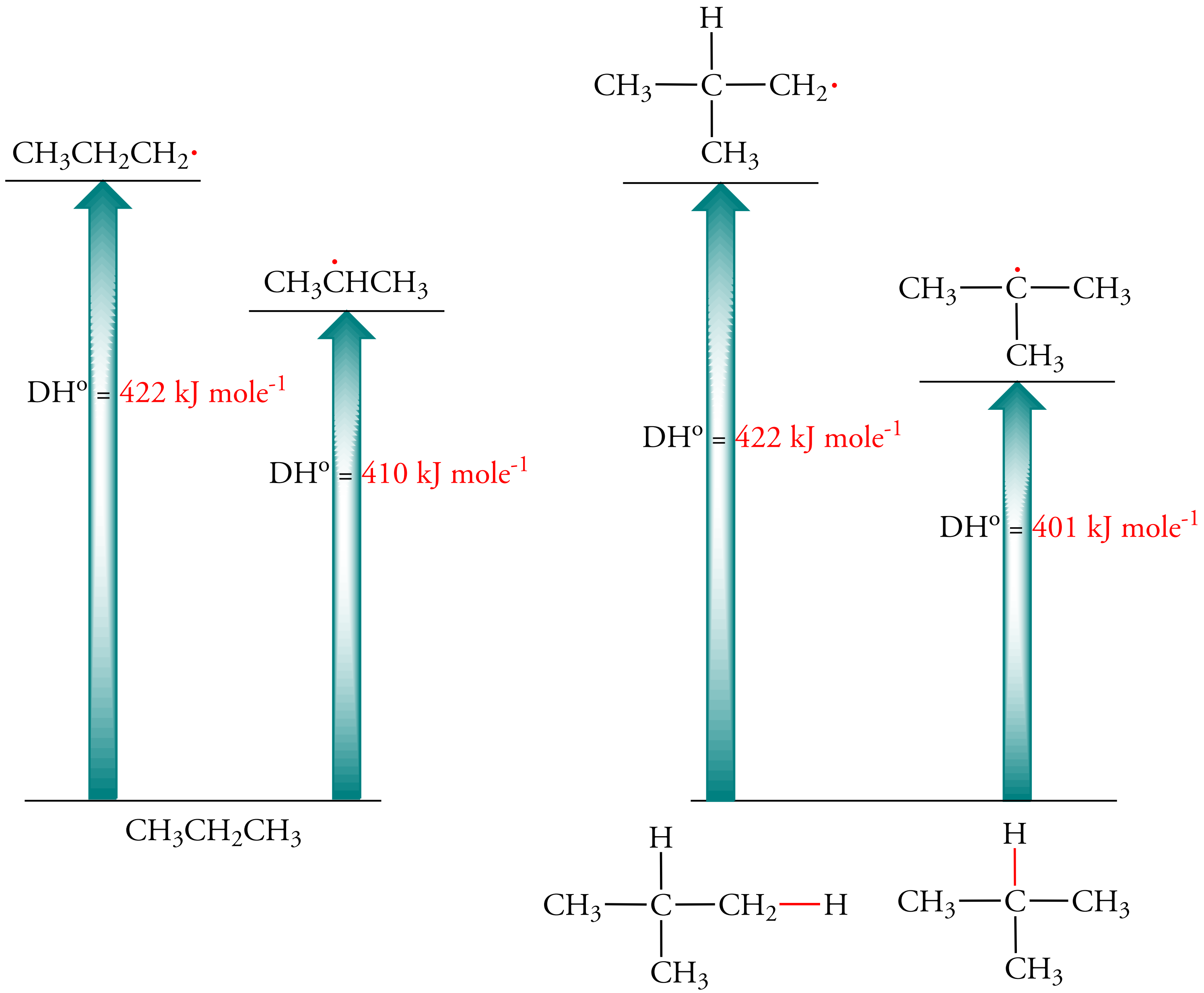
Bond	*DH°* (*kJ mol*$^{-1}$)	*Bond*	*DH°* (*kJ mol*$^{-1}$)
CH_3—H	438	CH_3—CH_3	368
CH_3CH_2—H	422	CH_3CH_2—CH_3	356
$CH_3CH_2CH_2$—H	422	$(CH_3)_2CH$—CH_3	351
$(CH_3)_2CH$—H	410	$(CH_3)_3C$—CH_3	335
$(CH_3)_3C$—H	401		

4.11 PHYSICAL PROPERTIES OF ALKANES

Figure 4.18 Relative Stabilities of Alkyl Radicals

(a) A secondary isopropyl radical is more stable than a primary *n*-propyl radical by 12 kJ mole^{-1}.

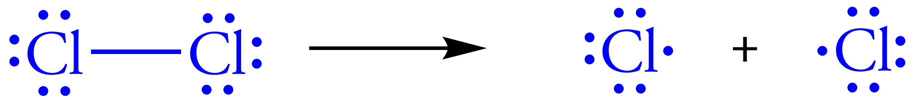
(b) A *tert*-butyl radical is 9 kJ mole^{-1} more stable than a secondary isopropyl radical, but the stabilities of the primary *n*-propyl and isobutyl radicals are the same.



4.13 CHLORINATION OF AN ALKANE— A RADICAL REACTION

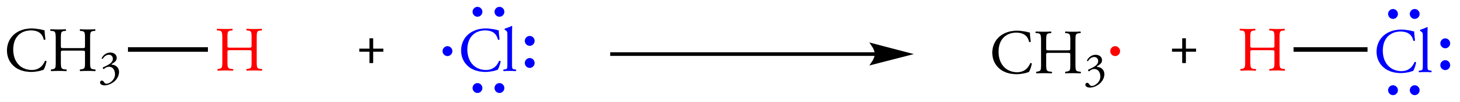
$$\mathrm{CH_3{-}H} + \mathrm{Cl{-}Cl} \longrightarrow \mathrm{CH_3{-}Cl} + \mathrm{H{-}Cl}$$

Step 1. **Initiation.**



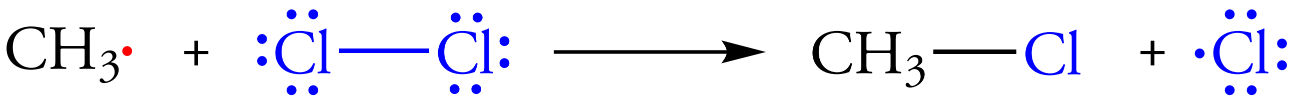
$$:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}{-}\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow :\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

Step 2. **Propagation.**



$$\mathrm{CH_3{-}H} + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{CH_3}\cdot + \mathrm{H}{-}\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

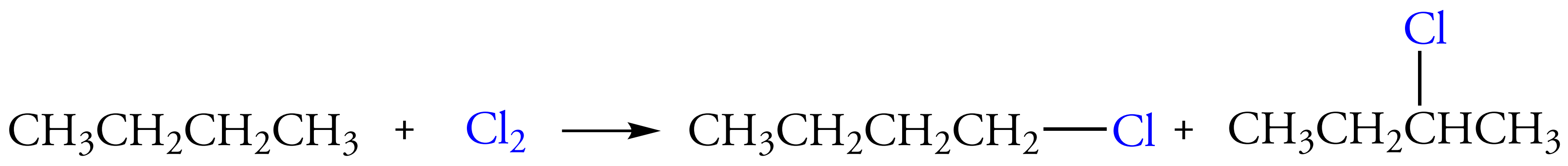
Step 3. **Propagation.**



$$\mathrm{CH_3}\cdot + :\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}{-}\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{CH_3{-}Cl} + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

$$\mathrm{CH_3}\cdot + \cdot\mathrm{CH_3} \xrightarrow{\text{radical chain termination}} \mathrm{CH_3{-}CH_3}$$

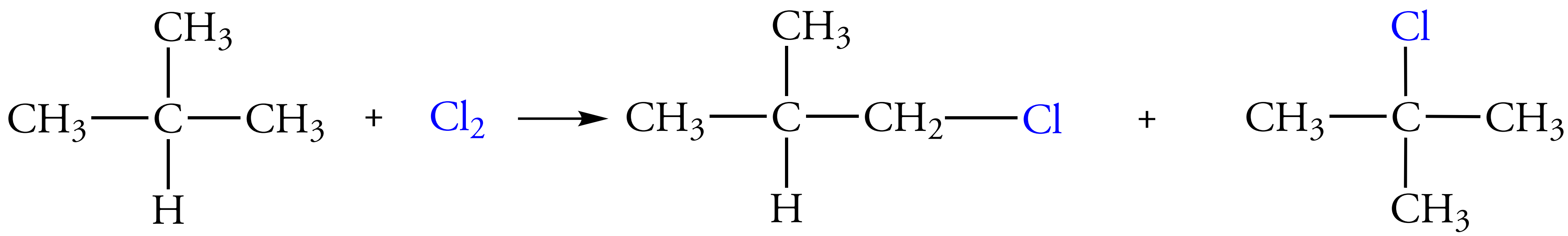
Regioselectivity of Alkane Halogenation-1



$$CH_3CH_2CH_2CH_3 + Cl_2 \longrightarrow CH_3CH_2CH_2CH_2{-}Cl + CH_3CH_2\overset{\overset{\displaystyle Cl}{|}}{C}HCH_3$$

1-chlorobutane
(28%)

2-chlorobutane
(72%)

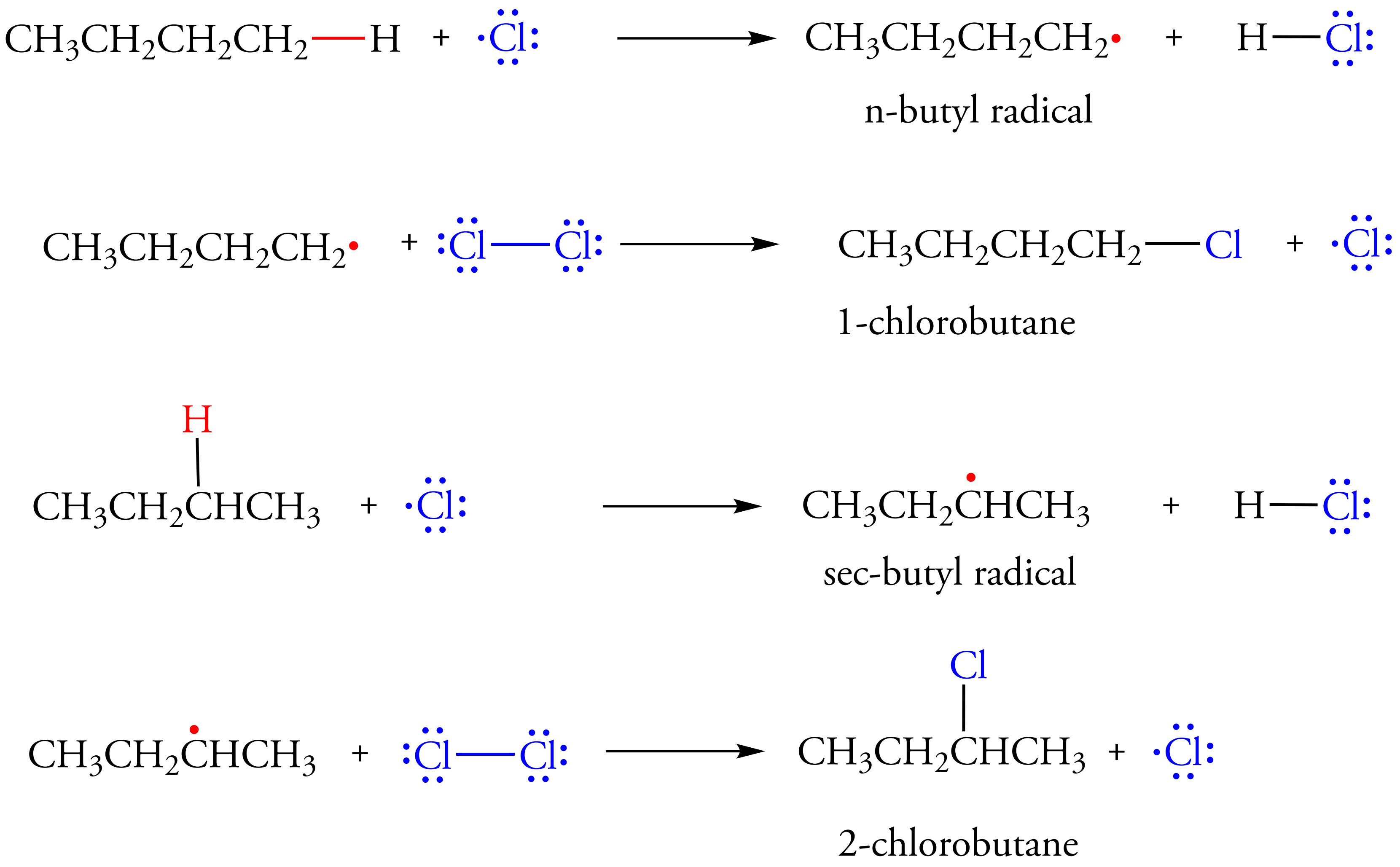


$$CH_3{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_3 + Cl_2 \longrightarrow CH_3{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_2{-}Cl + CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}{-}CH_3$$

1-chloro-2-methylpropane
(63%)

2-chloro-2-methylpropane
(37%)

Regioselectivity of Alkane Halogenation-2



$$CH_3CH_2CH_2CH_2{-}H + \cdot\ddot{\underset{..}{Cl}}\!: \longrightarrow CH_3CH_2CH_2CH_2\cdot + H{-}\ddot{\underset{..}{Cl}}\!:$$

n-butyl radical

$$CH_3CH_2CH_2CH_2\cdot + :\ddot{\underset{..}{Cl}}{-}\ddot{\underset{..}{Cl}}\!: \longrightarrow CH_3CH_2CH_2CH_2{-}Cl + \cdot\ddot{\underset{..}{Cl}}\!:$$

1-chlorobutane

$$CH_3CH_2\overset{\overset{H}{|}}{C}HCH_3 + \cdot\ddot{\underset{..}{Cl}}\!: \longrightarrow CH_3CH_2\dot{C}HCH_3 + H{-}\ddot{\underset{..}{Cl}}\!:$$

sec-butyl radical

$$CH_3CH_2\dot{C}HCH_3 + :\ddot{\underset{..}{Cl}}{-}\ddot{\underset{..}{Cl}}\!: \longrightarrow CH_3CH_2\overset{\overset{Cl}{|}}{C}HCH_3 + \cdot\ddot{\underset{..}{Cl}}\!:$$

2-chlorobutane

Reactivity and Statistical Factors-1

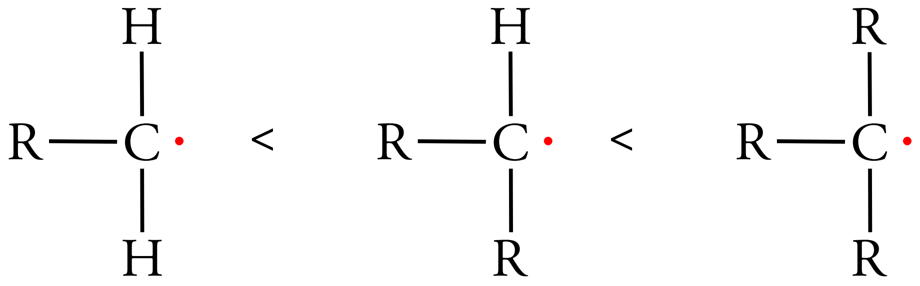
$$\frac{\text{\% 2-chlorobutane}}{\text{\% 1-chlorobutane}} = \frac{(\text{rate of } 2^{o} \text{ H abstraction}) \text{ x 4 atoms}}{(\text{rate of } 1^{o} \text{ H abstraction}) \text{ x 6 atoms}}$$

$$\frac{\text{rate of } 2^{o} \text{ H abstraction}}{\text{rate of } 1^{o} \text{ H abstraction}} = \frac{\text{\% 2-chlorobutane x 6 atoms}}{\text{\% 1-chlorobutane x 4 atoms}} = \frac{72 \text{ x } 6}{28 \text{ x } 4} = \frac{3.9}{1}$$

$$\frac{\text{\% 2-chloro-2-methylpropane}}{\text{\% 1-chloro-2-methylpropane}} = \frac{(\text{rate of } 3^{o} \text{ H abstraction}) \text{ x 1 atom}}{(\text{rate of } 1^{o} \text{ H abstraction}) \text{ x 9 atoms}}$$

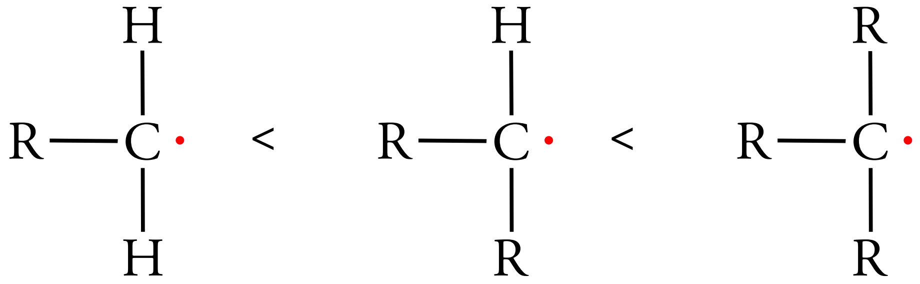
$$\frac{\text{rate of } 3^{o} \text{ H abstraction}}{\text{rate of } 1^{o} \text{ H abstraction}} = \frac{\text{\% 2-chloro-2-methylpropane x 9 atoms}}{\text{\% 1-chloro-2-methylpropane x 1 atoms}} = \frac{37 \text{ x } 9}{63 \text{ x } 1} = \frac{5.3}{1}$$

Reactivity and Statistical Factors-2



primary	secondary	tertiary
1	3.9	5.3

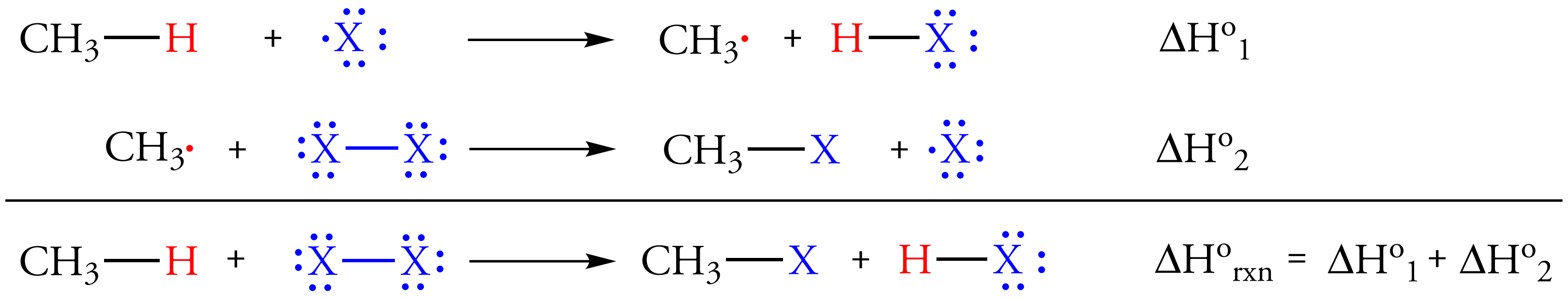
—— relative rate of chlorination ⟶



primary	secondary	tertiary
1	80	1650

—— relative rate of bromination ⟶

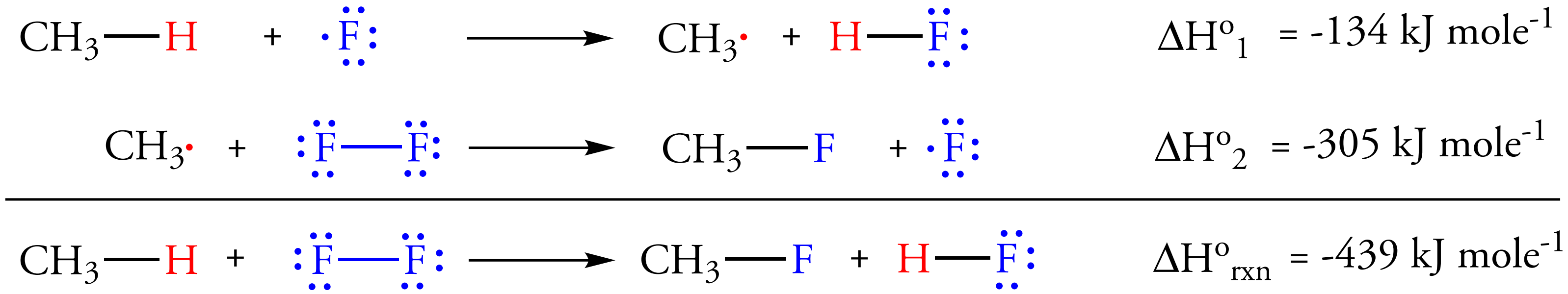
Enthalpy Changes for Halogenation Reactions-1



$$CH_3{-}H + \cdot X \longrightarrow CH_3\cdot + H{-}X \qquad \Delta H^o{}_1$$

$$CH_3\cdot + X{-}X \longrightarrow CH_3{-}X + \cdot X \qquad \Delta H^o{}_2$$

$$CH_3{-}H + X{-}X \longrightarrow CH_3{-}X + H{-}X \qquad \Delta H^o{}_{rxn} = \Delta H^o{}_1 + \Delta H^o{}_2$$

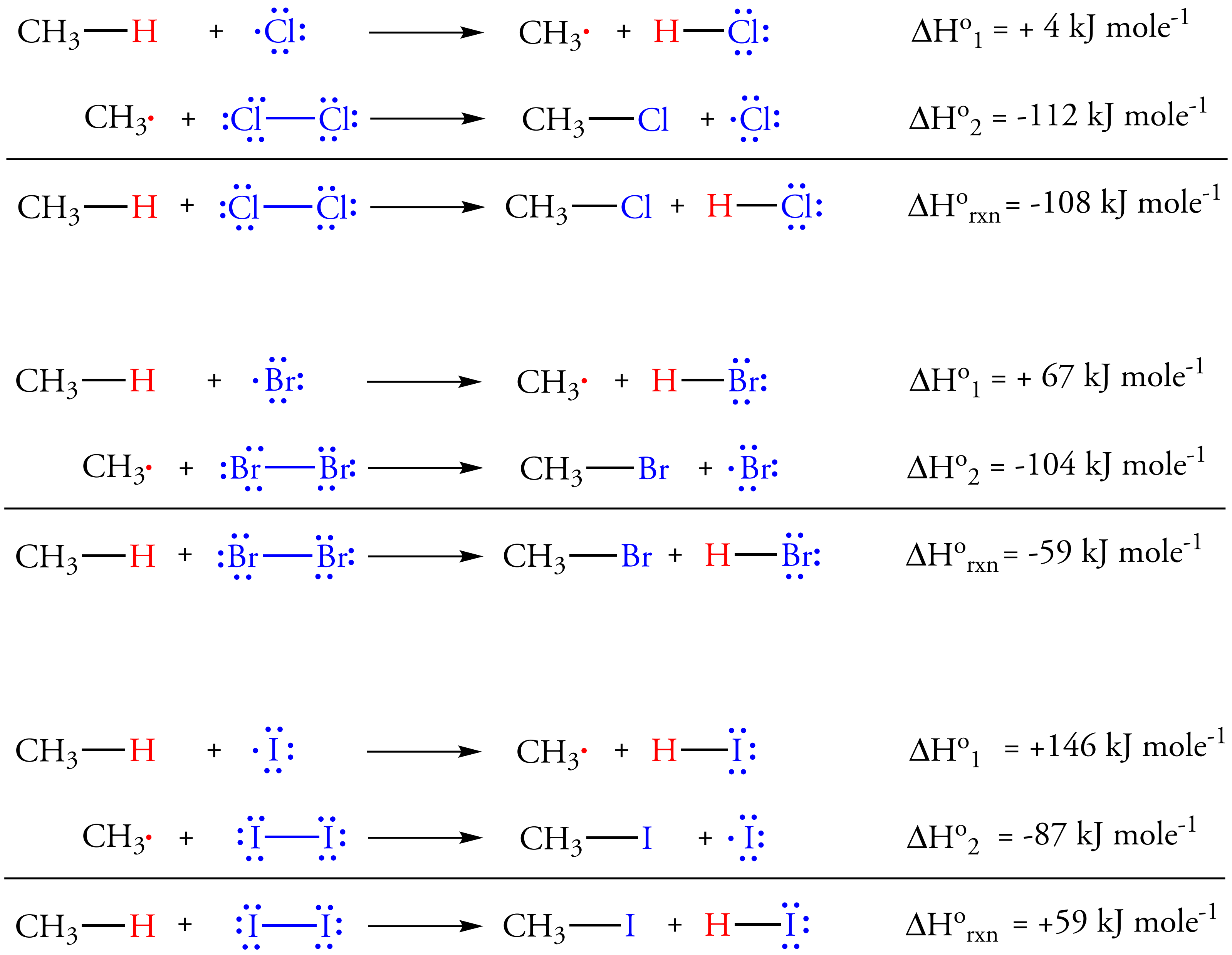


$$CH_3{-}H + \cdot F \longrightarrow CH_3\cdot + H{-}F \qquad \Delta H^o{}_1 = -134\ \mathrm{kJ\ mole^{-1}}$$

$$CH_3\cdot + F{-}F \longrightarrow CH_3{-}F + \cdot F \qquad \Delta H^o{}_2 = -305\ \mathrm{kJ\ mole^{-1}}$$

$$CH_3{-}H + F{-}F \longrightarrow CH_3{-}F + H{-}F \qquad \Delta H^o{}_{rxn} = -439\ \mathrm{kJ\ mole^{-1}}$$

Enthalpy Changes for Halogenation Reactions-2



$$CH_3{-}H + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow CH_3\cdot + H{-}\ddot{\underset{\cdot\cdot}{Cl}}: \qquad \Delta H^o_1 = +4\ kJ\ mole^{-1}$$

$$CH_3\cdot + :\ddot{\underset{\cdot\cdot}{Cl}}{-}\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow CH_3{-}Cl + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \qquad \Delta H^o_2 = -112\ kJ\ mole^{-1}$$

$$CH_3{-}H + :\ddot{\underset{\cdot\cdot}{Cl}}{-}\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow CH_3{-}Cl + H{-}\ddot{\underset{\cdot\cdot}{Cl}}: \qquad \Delta H^o_{rxn} = -108\ kJ\ mole^{-1}$$

$$CH_3{-}H + \cdot\ddot{\underset{\cdot\cdot}{Br}}: \longrightarrow CH_3\cdot + H{-}\ddot{\underset{\cdot\cdot}{Br}}: \qquad \Delta H^o_1 = +67\ kJ\ mole^{-1}$$

$$CH_3\cdot + :\ddot{\underset{\cdot\cdot}{Br}}{-}\ddot{\underset{\cdot\cdot}{Br}}: \longrightarrow CH_3{-}Br + \cdot\ddot{\underset{\cdot\cdot}{Br}}: \qquad \Delta H^o_2 = -104\ kJ\ mole^{-1}$$

$$CH_3{-}H + :\ddot{\underset{\cdot\cdot}{Br}}{-}\ddot{\underset{\cdot\cdot}{Br}}: \longrightarrow CH_3{-}Br + H{-}\ddot{\underset{\cdot\cdot}{Br}}: \qquad \Delta H^o_{rxn} = -59\ kJ\ mole^{-1}$$

$$CH_3{-}H + \cdot\ddot{\underset{\cdot\cdot}{I}}: \longrightarrow CH_3\cdot + H{-}\ddot{\underset{\cdot\cdot}{I}}: \qquad \Delta H^o_1 = +146\ kJ\ mole^{-1}$$

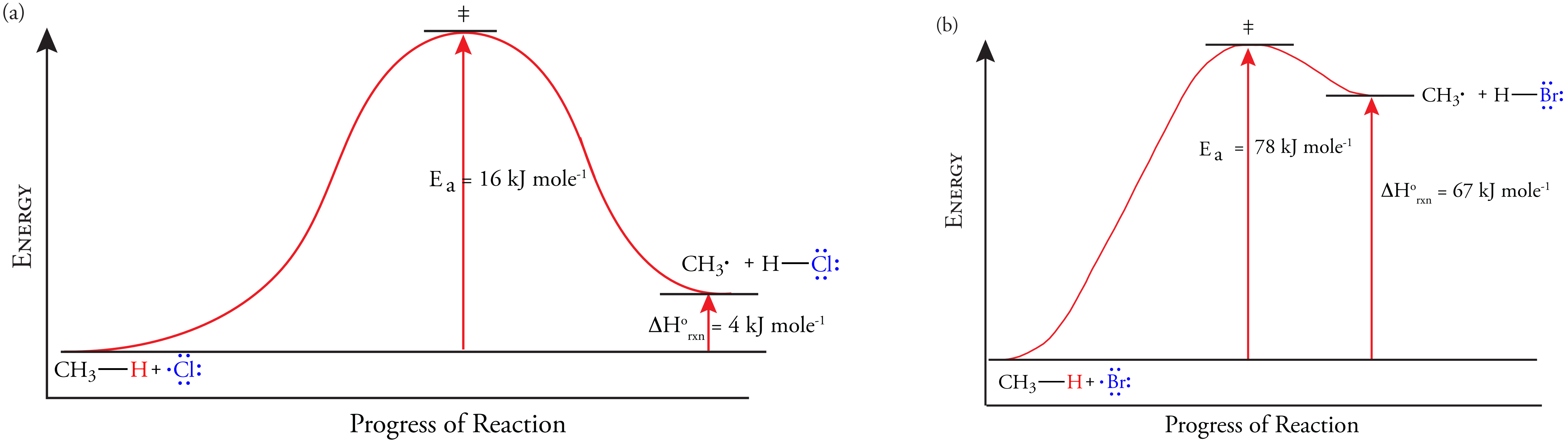
$$CH_3\cdot + :\ddot{\underset{\cdot\cdot}{I}}{-}\ddot{\underset{\cdot\cdot}{I}}: \longrightarrow CH_3{-}I + \cdot\ddot{\underset{\cdot\cdot}{I}}: \qquad \Delta H^o_2 = -87\ kJ\ mole^{-1}$$

$$CH_3{-}H + :\ddot{\underset{\cdot\cdot}{I}}{-}\ddot{\underset{\cdot\cdot}{I}}: \longrightarrow CH_3{-}I + H{-}\ddot{\underset{\cdot\cdot}{I}}: \qquad \Delta H^o_{rxn} = +59\ kJ\ mole^{-1}$$

Activation Energy for Halogenation

Figure 4.19 Potential Energy Diagrams for Halogenation Reactions

The energy of activation for the abstraction of a hydrogen atom by a chlorine atom (a) is smaller than the energy of activation for the abstraction of a hydrogen atom by a bromine atom (b).



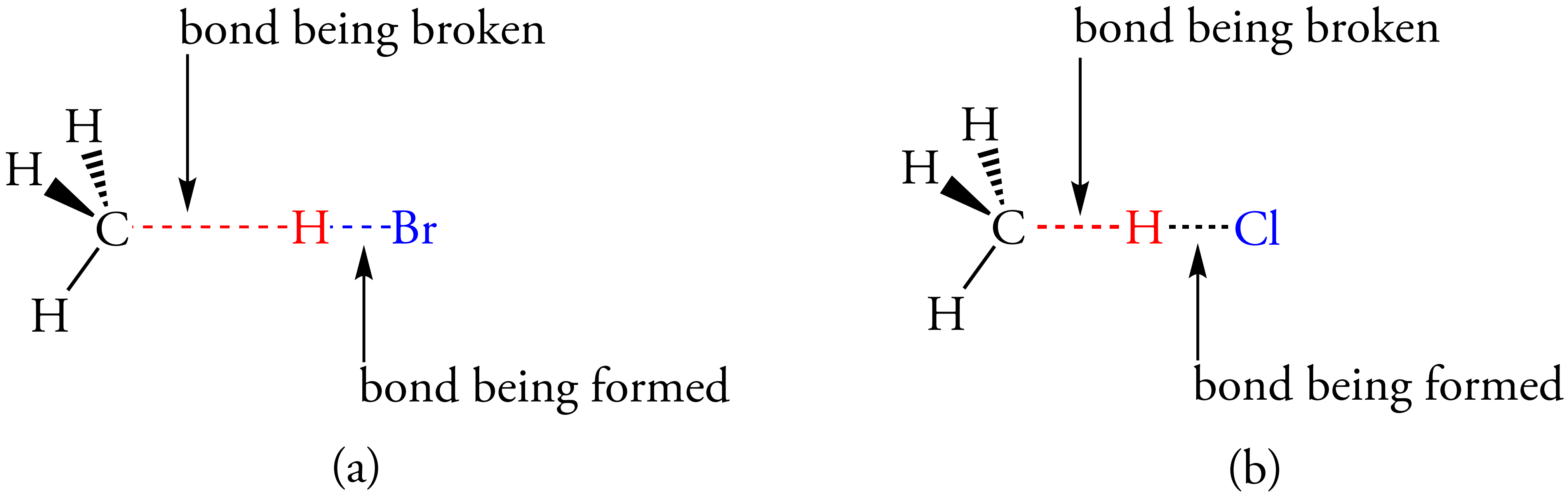
(a)

(b)

Figure 4.20 Transition State Structures for Halogenation Reactions

(a)In the transition state for abstraction of hydrogen by a bromine atom the C—H bond is mostly broken and the H—Br bond mostly formed.

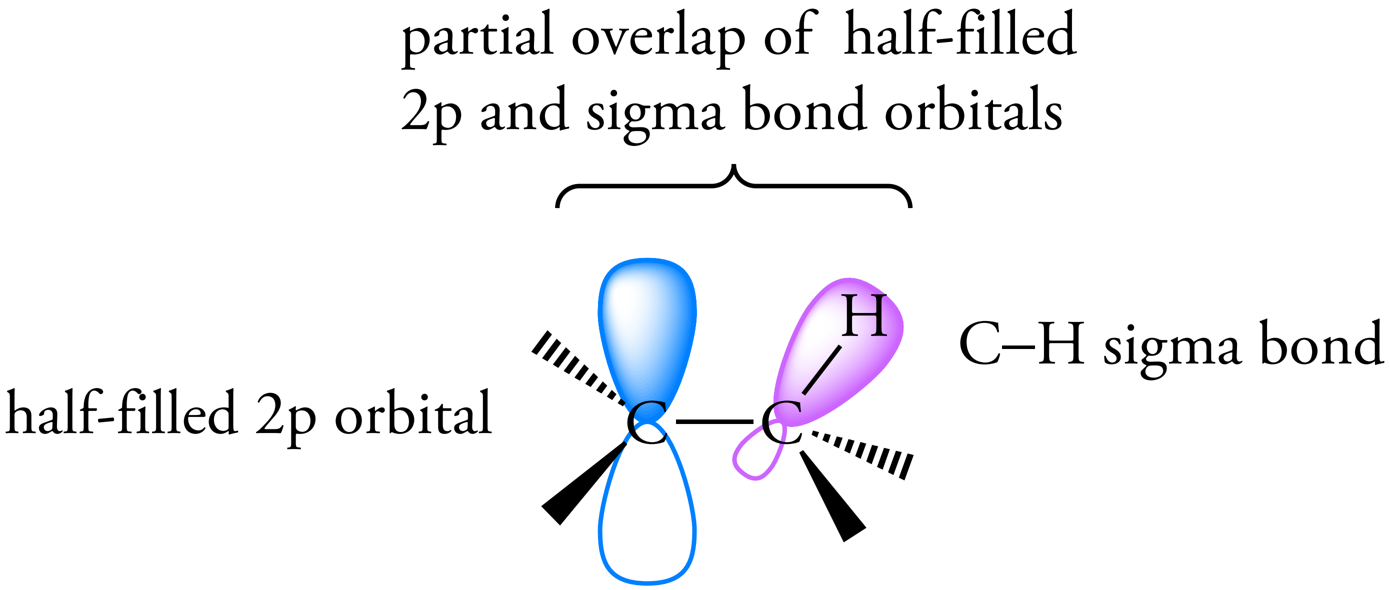
(b) In the transition state for abstraction of hydrogen by a chlorine atom, the C—H bond is broken to a lesser degree, and the H—Cl bond is only partially formed. The transition state for any reaction is the point of maximum energy on the minimum energy pathway; it is a saddle point.



Hyperconjugation

Figure 4.21 Hyperconjugation

A carbon radical is stabilized by overlap of the sigma orbital of a C—H bond on an adjacent carbon with the half-filled 2p orbital at the radical center. This phenomenon is called hyperconjugation.



partial overlap of half-filled
2p and sigma bond orbitals

half-filled 2p orbital

C–H sigma bond